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A Thermodynamic Model for the Solubility of Acid Gases in Treating Solutions

by

© Rajeev Dattatraya Deshmukh

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF Master of Science

IN

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled A Thermodynamic Model for the Solubility of Acid Gases in Treating Solutions submitted by Rajeev Dattatraya Deshmukh in partial fulfilment of the requirements for the degree of Master of Science in Chemical Engineering.

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Supervisor

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Date . 8 November 1978

ABSTRACT

A thermodynamic model has been developed for the solubility of acid gases in alkanolamine solutions. The model is based on the extended Debye-Huckel theory of electrolyte solutions. The interaction parameters are obtained from the equilibrium solubility data for the pure acid gases and their mixtures. The model was used to correlate the solubility of carbon dioxide, hydrogen sulfide, and their mixtures in monoethanolamine, diethanolamine and diisopropanolamine solutions, in the temperature range of 25 to 120°C. The predicted partial pressures are in good agreement with the experimental data. However, the agreement for the partial pressures of carbon dioxide over 3.5 *N* DEA solutions is not satisfactory.

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NOMENCLATURE

a - Activity
a - Ratio of activities (amine to water)
b - A constant in Debye-Huckel theory
c - Concentration, kmol/m^3
c - Total number of moles, mol
d - Differential
m - Molality, mol/kg-solvent
n - Number of moles, mol
u - Mole ratio
x - Mole fraction in the liquid phase
y - Mole fraction in the vapor phase
z - Electric charge, in units of electronic charge
B - Array of interaction parameters
C - Deviations in predictions
C - Number of components
E - Errors in prediction
E - Number of components
G - Gibbs free energy, J
H - Henry's constant
K - Equilibrium constant
P - Pressure, Pa
P - Array of predictions
Q - Heat, J
R - Gas constant, J/mol K
S - Entropy, J/K
T - Temperature, K
U - Internal energy, J
V - Volume, m^3
W - Work, J
Y - Chemical formula

Greek letters

α - Stoichiometric coefficient
α - Mole ratio in liquid
β - Binary interaction parameter
γ - Activity coefficient
λ - Lagrange multiplier
μ - Chemical potential, J/mol
ϕ - Fugacity coefficient

Δ - A small perturbation
Π - Product sign
Σ - Summation sign

Subscripts

bh - Acidic dissociation of amine
i - Component i
i - Dissociation of amine
j - Element j
r - Reaction r
A - Carbamate formation
M - Carbamate formation
W - Water
0 - Solvent
1C - Ionization of hydrogen sulfide
2C - Dissociation of bisulfide ion
1Y - Ionization of carbon dioxide
2Y - Dissociation of bicarbonate ion
+ - Positively charged species
- - Negatively charged species

Superscripts

0 - Reference state
L - Liquid phase
V - Vapor phase

Symbol

[. . .] - Concentration, kmol/m^3

I. INTRODUCTION

Natural and manufactured gases frequently contain objectionable impurities like hydrogen sulfide and carbon dioxide, with small quantities of mercaptans, carbon monoxide, hydrocyanic acid, carbon disulfide and carbonyl sulfide. Hydrogen sulfide is particularly undesirable on account of its toxicity and corrosiveness. Removal of carbon dioxide is necessary if the gas is to be liquefied or used in a chemical process.

Aqueous solutions of alkanolamines are the most widely employed solvents for the absorption of carbon dioxide and hydrogen sulfide. The use of alkanolamines for the removal of acid gases was first suggested by Bottoms (1931) who discovered that

> "certain amines and amino compounds have the property of absorbing carbon dioxide and hydrogen sulfide, forming pyrolytically unstable carbonates and hydrosulfides which, when heated to a temperature above 50°C, decompose and liberate the carbon dioxide and hydrogen sulfide and release the free base in its original form."

The alkanolamines are characterized by the presence of the hydroxyl group -OH, and the amino group $-NH_2$. The hydroxyl group reduces the vapor pressure of the amine and increases its water solubility, while the amino group provides the necessary reactivity with the acid gases (Kohl and Riesenfeld, 1974).

Triethanolamine (TEA) was the first to be used, but it has been superseded by monoethanolamine (MEA) and diethanolamine (DEA). These amines have a higher capacity, higher reactivity and better thermal stability than TEA. DEA is the preferred solvent for gases containing carbonyl sulfide because MEA reacts irreversibly with carbonyl sulfide. Diisopropanolamine (DIPA) is used in the Adip process and the Sulfinol process. Methyldiethanolamine (MDEA) is a selective absorbent for hydrogen sulfide in the presence of carbon dioxide. Diglycolamine (DGA), which is a hydroxyaminoether (and not a true alkanolamine), has a lower vapor pressure than MEA. It can be used in high concentrations, resulting in higher acid gas pickup, lower steam consumption and a decrease in the amount of solution circulated. Table 1 shows the structural formulas, molecular weights and the chemical names of these amines.

The basic flow scheme for the acid gas removal process is shown in Figure 1. The sour gas is passed upward through the absorber, countercurrent to the amine solution. The sweetened gas leaves the top of the absorber and is dehydrated before being put to use. The rich solution from the bottom of the absorber is heated in the amine-amine heat exchanger and fed to the top tray of the stripping column. The rich solution flows down the stripping column in countercurrent contact with the vapor generated in the reboiler and is stripped of the acid gases. Some of the lean solution leaving the stripping column is sent to the reboiler. The remaining solution, together with the condensate from the reboiler is passed through the amine-amine heat exchanger and a cooler before being fed to the top tray of the absorber. The acid gas leaving the stripping column is cooled to condense the water vapor. The

condensate is separated in the separator and is fed back at the top of the stripping column.

This basic scheme may be modified by including (1) water wash of the purified gas for amine recovery, (2) flashing of the rich solution to remove dissolved hydrocarbons or (3) split-stream flow to reduce the steam requirement.

Over the past fifty years, several investigators have measured the equilibrium solubility of acid gases in alkanolamine solutions. Kohl and Riesenfeld (1974) and Lee *et al.* (1973) have presented literature reviews.

The rates of absorption and stripping depend upon the departure from equilibrium in the absorber and the stripping column. Accurate equilibrium data are essential for the proper design of the gas removal process. The solubility data have customarily been published as the plots of the acid gas partial pressure against the mole ratio in liquid (acid gas/amine), at a given temperature and amine concentration. The solubility of the mixtures is also expressed in the same fashion, with the mole ratio of the other acid gas as a parameter.

These data are useful in many ways. They can be used to calculate the acid gas loadings at given partial pressures, the minimum circulation rate of the amine solution and the number of trays in the absorber and the stripping column. In existing plants, these data may be used to determine how close the absorber is to equilibrium at the lean end and if a pinch condition exists at the rich end. As the amine solution flows down the absorber, its temperature increases because of the heat released by the absorption of acid gases. Therefore, the solubility data are needed for many different temperatures. The effort required to collect these data and the wide range of process conditions make a computer-oriented correlation of the data highly desirable. This correlation would be useful for interpolating the solubility data to temperatures, loadings or amine concentrations where no data are available.

Simple curve fitting is unsuitable because it provides no insight into the physical basis for solubility and it can not be used with confidence at extremes of loadings or pressures. Such a model would be inflexible and difficult to maintain as new data could not be easily incorporated into it. The model would contain a large number of meaningless coefficients. The nature of interpolation is also not obvious. For example, it is not obvious whether the same functions should be used for interpolating over temperatures as those used for interpolating over normalities.

A thermodynamic model based on the physical processes occurring in the system would certainly be preferable to the curve fitting approach. This model would be able to correlate the solubility data by making realistic approximations. Recently, two models have been proposed to correlate the equilibrium data for acid gas / alkanolamine systems. Before analyzing these models in detail, it is necessary to understand the thermodynamic criteria for equilibrium in multicomponent, multiphase systems.

Table 1. Alkanolamines

(1) Monoethanolamine
Abbreviation : MEA
Chemical formula : $H_2NCH_2CH_2OH$
IUPAC name : 2-aminoethanol
Molecular weight 61.09

(2) Diethanolamine
Abbreviation : DEA
Chemical formula : $HN(CH_2CH_2OH)_2$
IUPAC name : 2,2'-dihydroxydiethylamine
Molecular weight 105.14

(3) Triethanolamine
Abbreviation : TEA
Chemical formula : $(HOCH_2CH_2)_3N$
IUPAC name : 2,2',2"-trihydroxytriethylamine
Molecular weight 149.19

(4) Diisopropanolamine
Abbreviation : DIPA
Chemical formula : $[CH_3CH(OH)CH_2]_2NH$
IUPAC name : 2,2'-dihydroxydipropylamine
Molecular weight 133.19

(5) Diglycolamine
Abbreviation : DGA
Chemical formula : $HOCH_2CH_2OCH_2CH_2NH_2$
IUPAC name : 2,2'-hydroxyaminoethylether
Molecular weight 105.14

(6) Methyldiethanolamine
Abbreviation : MDEA
Chemical formula : $(HOCH_2CH_2)_2NCH_3$
IUPAC name : 2,2'-dihydroxydiethylmethylamine
Molecular weight 119.17

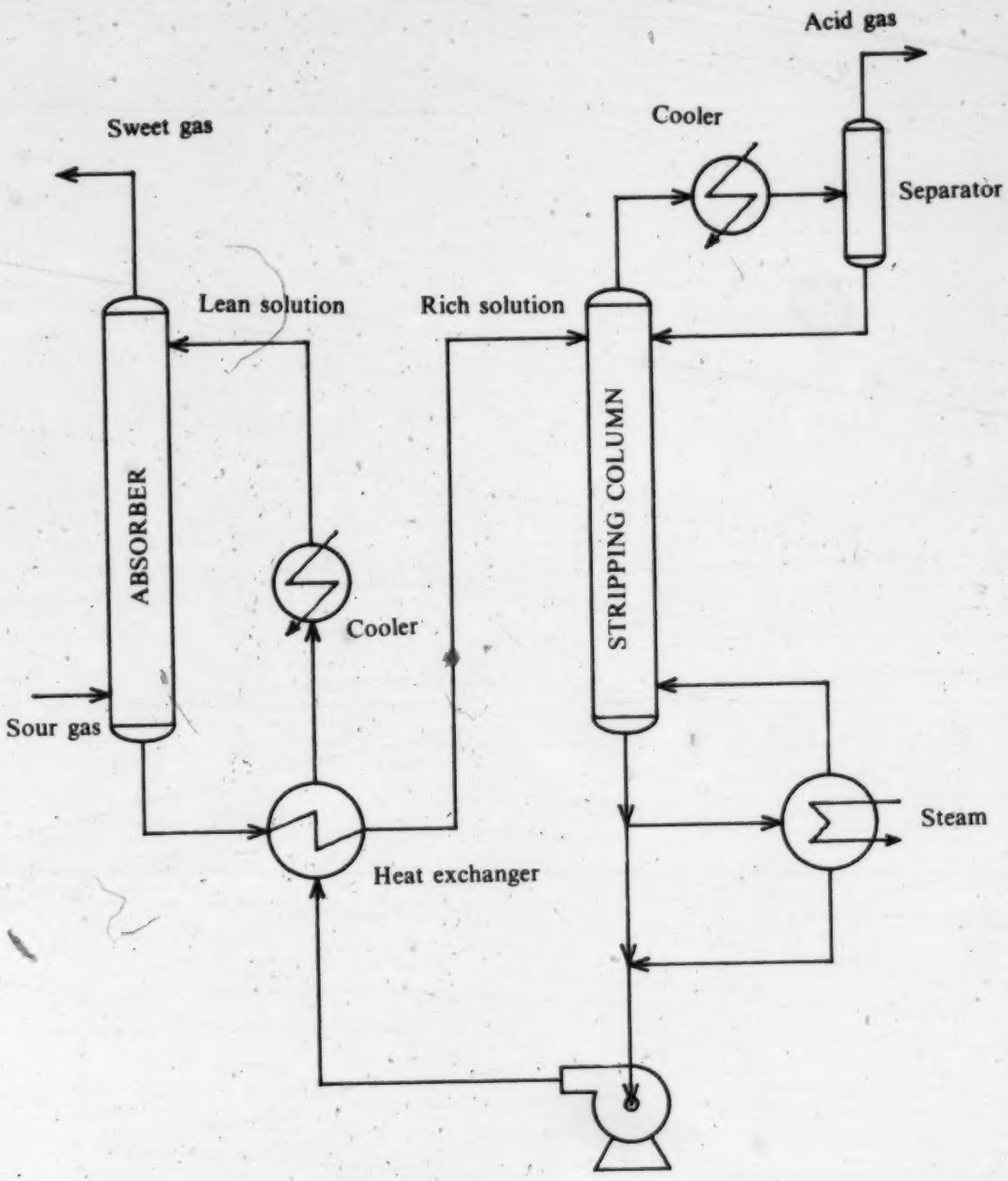

Figure 1. Acid Gas Removal Process

II. THERMODYNAMIC FRAMEWORK

The criteria for equilibrium can be derived from the laws of thermodynamics. These criteria allow us to examine the assumptions implicit in various solubility models and point the way to areas where improvements can be made.

The second law of thermodynamics states that

$$dS + dS_{surr} \geq 0$$

If dQ is the heat added to the system,

$$dS_{surr} = - dQ / T$$

The first law of thermodynamics for closed systems is

$$dQ = dU - dW$$

If only mechanical work is performed on the system, — (2.1)

$$dW = - P\, dV$$

These equations can be combined to give

$$dS - (dU + P\, dV) / T \geq 0$$

This can be stated in the form

$$dU + P\, dV - T\, dS \leq 0$$

as T is never less than zero. The Gibbs free energy, G, is defined by

$$G = U + P\, V - T\, S$$

At a constant temperature and pressure,

$$dG = dU + P\, dV - T\, dS$$

The second law can now be stated in terms of the Gibbs free energy, — (2.2)

$$(dG) \leq 0 \text{ at constant T and P}$$

Any change occurring within the system has to satisfy this condition. A state of equilibrium is attained when G reaches its minimum value. Further change is impossible as this change would not satisfy Equation (2.2).

For a p-phase system consisting of C components, the fundamental equation can be written in the form $i = 1, \ldots, C; \pi = 1, \ldots, p$

$$G = G (T, P, n_i^{\pi})$$

where n_i^{π} is the number of moles of the component i in the phase π. The chemical potential μ_i^{π} is defined by

$$\mu_i^{\pi} = \partial G / \partial n_i^{\pi}$$

In this expression, the partial derivative is taken with respect to n_i^{π}, keeping the temperature, pressure and the number of moles of each component in every phase (except n_i^{π}) constant.

The Gibbs free energy is an extensive property of the system.

$$G (T, P, k\, n_i^{\pi}) = k\, G (T, P, n_i^{\pi})$$

Applying Euler's theorem, we have

$$G = \Sigma\, n_i^{\pi}\, \mu_i^{\pi}$$

Therefore,

$$dG = \Sigma\, n_i^{\pi}\, d\mu_i^{\pi} + \Sigma\, \mu_i^{\pi}\, dn_i^{\pi}$$

However, differentiating the fundamental equation,

$$dG = \Sigma\, \mu_i^{\pi}\, dn_i^{\pi}$$

These two equations yield the Gibbs-Duhem equation

$$\Sigma\, n_i^{\pi}\, d\mu_i^{\pi} = 0$$

In the state of equilibrium, G is minimum and the variations in G, caused by small variations in n_i^{π} must be zero. The variations dn_i^{π} are not independent because they have to satisfy additional constraints such as mass balance, charge balance, non-negativity, etc.. The solution to this constrained minimization problem requires Lagrange multipliers.

Let u_{ij} be the moles of element j in one mole of component i and let c_j be the total number of moles of element j present in the system. If E is the number of different chemical elements present in the system, the mass balance can be written as

$$\Sigma\, n_i^{\pi}\, u_{ij} - c_j = 0 \qquad \text{— (2.3)}$$

The charge balance can be expressed in this form, with $c_{E+1} = 0$ and $u_{i,E+1}$ = the charge on the i-th species.

An augmented function G_A can be defined as

$$G_A = G + \Sigma\, \lambda_j \left(\Sigma\, n_i^{\pi}\, u_{ij}\, c_j \right)$$

The condition of equilibrium now becomes

$$\delta G_A = 0$$

Therefore,

$$\Sigma\, \mu_i^{\pi}\, dn_i^{\pi} + \Sigma\, d\lambda_j \left(\Sigma\, n_i^{\pi}\, u_{ij} - c_j \right) + \Sigma\, \lambda_j \left(\Sigma\, u_{ij}\, dn_i^{\pi} \right) = 0$$

And thence,

$$\Sigma \left(\mu_i^{\pi} + \Sigma\, \lambda_j\, u_{ij} \right) dn_i^{\pi} + \Sigma \left(\Sigma\, n_i^{\pi}\, u_{ij} - c_j \right) d\lambda_j = 0$$

As dn_i^{π} and $d\lambda_j$ are independent variables, each coefficient in the above equation must be zero.

$$\therefore\ \mu_i^{\pi} + \Sigma\, \lambda_j\, u_{ij} = 0 \qquad \text{— (2.4)}$$

(and $\Sigma\, n_i^{\pi}\, u_{ij} - c_j = 0$, which gives back the constraint equations). These equations can be solved for n_i^{π} and λ_j to obtain the equilibrium composition and the Lagrange multipliers.

Traditionally, thermodynamicists have avoided the use of artificial variables, λ_j, by postulating chemical reactions. The reactions are expressed as

$$\Sigma\, \alpha_i^{\pi}{}_r\, Y_i^{\pi} = 0$$

where Y_i^{π} is the chemical formula for the i-th component. The superscript π indicates the phase in which the reaction is taking place. The coefficients $\alpha_i^{\pi}{}_r$ are called the stoichiometric coefficients for the reaction r. By convention, $\alpha_i^{\pi}{}_r$ are positive for the products of the reaction and negative for the reactants. These postulated reactions allow us to eliminate λ_j from the criterion of equilibrium.

Any postulated chemical equations have to be consistent with the constraints mentioned earlier. The coefficients $\alpha_i^{\pi}{}_r$ have to satisfy the equation

$$\Sigma\, u_{ij}\, \alpha_i^{\pi}{}_r = 0 \qquad \text{— (2.5)}$$

i.e. every postulated chemical equation has to conserve the mass of each element and the electric charge. Multiplying Equation (2.4) by $\alpha_i^{\pi}{}_r$ and summing,

$$\Sigma\, \alpha_i^{\pi}{}_r\, \mu_i^{\pi} + \Sigma\, \lambda_j \left(\Sigma\, u_{ij}\, \alpha_i^{\pi}{}_r \right) = 0$$

From Equation (2.5), the second term is zero.

$$\Sigma\ \alpha_i^{\pi}{}_r\ \mu_i^{\pi} = 0 \qquad \text{— (2.6)}$$

This equation expresses the condition for phase and reaction equilibria in a closed system at a constant temperature and pressure.

Since it is difficult to visualize chemical potentials, the criteria for equilibrium are often expressed in terms of activities, defined by

$$\mu_i^{\pi} = \mu_i^{0\pi} + RT\ ln\ a_i^{\pi} \qquad \text{— (2.7)}$$

where a_i^{π} is the activity and $\mu_i^{0\pi}$ the reference value of the chemical potential. The reference state is the one of unit activity.

The condition of equilibrium in terms of activities is

$$\Sigma\ \alpha_i^{\pi}{}_r\ (\ \mu_i^{0\pi} + RT\ ln\ a_i^{\pi}\ ) = 0$$

$$\therefore\ \Sigma\ \alpha_i^{\pi}{}_r\ ln\ a_i^{\pi} = -\ \Sigma\ \alpha_i^{\pi}{}_r\ (\ \mu_i^{0\pi}\ /\ RT\ ) \qquad \text{— (2.8)}$$

The right hand side depends only on the reference states chosen and is a constant at a prescribed temperature.

Equation (2.8) is the starting point for most studies of phase and reaction equilibria. The vapor-liquid equilibrium (VLE) is given by

$$Y_i\ (\text{liquid}) = Y_i\ (\text{vapor})$$

The condition for equilibrium is

$$ln\ a_i^{V} - ln\ a_i^{L} = (\ \mu_i^{0L} - \mu_i^{0V}\ )\ /\ RT$$

$$a_i^{V}\ /\ a_i^{L} = exp\ (\ (\ \mu_i^{0L} - \mu_i^{0V}\ )\ /\ RT\ )$$

The right hand side is called the Henry's constant, H_i.

$$a_i^{V} = H_i\ a_i^{L} \qquad \text{— (2.9)}$$

The Henry's constant depends only upon the reference states. This equation can be further modified by introducing two coefficients, ϕ_i and γ_i. The fugacity coefficient, ϕ_i, is defined by

$$a_i^{V} = \phi_i\ y_i\ P\ /\ (\ \phi_i\ y_i\ P\ )^0$$

and

$$\phi_i \rightarrow 1 \text{ as } P \rightarrow 0.$$

If the reference state is chosen so that

$$\phi_i^0 = 1,\ y_i^0 = 1 \text{ and } P^0 = 1,$$

we get

$$a_i^{V} = \phi_i\ y_i\ P \qquad \text{— (2.10)}$$

We thus get a rather simple expression for the activity if the reference state is that of the *perfect* pure gas at the system temperature and unit pressure. This state is only hypothetical because ϕ_i will be, in general, different from unity at finite pressures. Also the expression

$$a_i^{V} = \phi_i\ y_i\ P$$

is meaningful only if P is measured in the same system of units in which P^0 is unity. For example, if P^0 is 1 atm, P has to be expressed in atmospheres.

The fugacity coefficient has been defined in such a way that for an ideal mixture of perfect gases, $\phi_i = 1$. There is no perfect liquid law and hence no preferred definition for the activity coefficient, γ_i. The activity coefficient is defined in several ways, one of which is

$$a_i^{L} = \gamma_i\ m_i\ /\ \gamma_i^0\ m_i^0$$

And when $\Sigma\ m_i \rightarrow 0$,

$$\gamma_i \rightarrow 1 \text{ for solutes}$$

and

$\gamma_0 \rightarrow 1$ for the solvent.

Other units of concentration such as molarity, normality or mole fraction can be used in place of molality. These lead to activity coefficients different from those defined above. It is clear from the definition that the activity coefficients tend to unity in an infinitely dilute solution. The reference state is that of a hypothetical infinitely dilute solution of *unit* molality. This leads to a simple expression

$$a_i = \gamma_i \, m_i \qquad \text{— (2.11)}$$

It must be emphasized that m_i is in the same set of units in which m_i^0 is unity. In Equation (2.11), m_i is a dimensionless number.

With these definitions, the VLE relation becomes

$$\phi_i \, y_i \, P = H_i \, \gamma_i \, m_i \qquad \text{— (2.12)}$$

By convention, the activity coefficient of water has been based on its mole fraction rather than molality. The reference state is that of pure water at the system temperature and pressure. The VLE relation for water is

$$\phi_w \, y_w \, P = H_w \, \gamma_w \, x_w \qquad \text{— (2.13)}$$

The mole fraction of water is usually close to unity so that $\gamma_w = 1$. For liquid water in equilibrium with its vapor, $x_w = 1$ and $y_w = 1$. At low pressures, the fugacity coefficient is also close to unity. Thus the Henry's constant of water is equal to its vapor pressure. This conclusion is valid if the temperature is less than 150°C and if the mole fraction of water in the liquid phase is close to unity.

For aqueous phase chemical reactions, the condition for equilibrium is

$$\Sigma \, \alpha_{ir} \, ln \, a_i = - \Sigma \, \alpha_{ir} \, (\mu_i^0 \, / \, RT)$$

or

$$\Pi \, (a_i) \, ** \, \alpha_{ir} = exp \, [- \Sigma \, \alpha_{ir} \, (\mu_i^0 \, / \, RT)]$$

The right hand side is called the equilibrium constant, K_r for the reaction r. Like H_i, this dimensionless constant depends only upon the reference states.

$$K_r = \Pi \, (a_i) \, ** \, \alpha_{ir} \qquad \text{— (2.14)}$$

where

$a_i = \gamma_i \, m_i$ for solutes

and

$a_w = x_w$ for water.

Equations (2.12), (2.13) and (2.14) describe the conditions for equilibrium in an aqueous solution in contact with its vapor. To be able to use these equations, we need information about ϕ_i and γ_i for all the components present in the system, as well as the Henry's constants and the equilibrium constants. When this information is available from experiments, it can be used to predict the equilibrium composition. In absence of detailed information, we have to construct simple models which will help us extract this information from the incomplete data.

III. SOLUBILITY MODELS

The first attempt to correlate the solubility data for the CO_2 / amine / water system was made by Mason and Dodge (1936). They found equations

> "which represented the data fairly well over a limited range of conditions but all attempts to broaden the applicability resulted in such complexity that it defeated the purpose for which the equation was intended."

Although Mason and Dodge do not describe the method they used, it is evident that they adopted a curve fitting approach. The reactions between alkanolamines and carbon dioxide had not been studied at that time.

Van Krevelen *et al.* (1949) developed a method for predicting the vapor pressures of hydrogen sulfide and ammonia over aqueous solutions. Their scheme was later used by Danckwerts and McNeil (1967) for the CO_2 / amine / water system. Kent and Eisenberg (1975) used a modification of this method to correlate the equilibrium solubilities in CO_2 / H_2S / amine / water system.

Another model developed from the work of Atwood *et al.* (1957) who proposed a method for calculating equilibrium composition in the H_2S / amine / water system. Their method was generalized by Klyamer *et al.* (1973) and applied to the CO_2 / H_2S / amine / water system. A modification of this method was suggested by Nasir (1975). Edwards *et al.* (1975) used the extended Debye-Huckel theory of electrolyte solutions to calculate the liquid-phase activity coefficients. They also devised a method to obtain the parameters required in their model. Recently, Beutier and Renon (1978) have improved Edwards' method by a more accurate representation of activity coefficients.

All these models are based on the chemical reaction equilibria in the liquid phase. The main reactions occurring in the CO_2 / H_2S / amine / water system are as follows:

Ionization of water:

$$H_2O = H^+ + OH^- \qquad \text{— (3.1)}$$

Dissociation of hydrogen sulfide:

$$H_2S = H^+ + HS^- \qquad \text{— (3.2)}$$

Dissociation of carbon dioxide:

$$H_2O + CO_2 = H^+ + HCO_3^- \qquad \text{— (3.3)}$$

Dissociation of alkanolamine:

$$H_2O + RR'NH = RR'NH_2^+ + OH^- \qquad \text{— (3.4)}$$

Formation of carbamate:

$$RR'NH + CO_2 = RR'NCOO^- + H^+ \qquad \text{— (3.5)}$$

Dissociation of bisulfide ion:

$$HS^- = H^+ + S^= \qquad \text{— (3.6)}$$

Dissociation of bicarbonate ion:

$$HCO_3^- = H^+ + CO_3^= \qquad \text{— (3.7)}$$

In these equations RR'NH is the chemical formula of the alkanolamine. Tertiary amines (TEA and MDEA) lack the extra hydrogen atom and do not form carbamates by reaction 5. In addition to the reactions 1 to 7, other reactions may take place in the solution. The amines react with carbon dioxide to form heterocyclic compounds. The amines may react with impurities in the sour gas such as carbonyl sulfide and carbon disulfide. These reactions have little effect on the acid gas equilibria as only a small fraction of the reactants is used up in these reactions. The alkanolamines have two active groups, viz. $-NH_2$ and $-OH$. On account of this bifunctional nature of alkanolamines, the following reactions are possible:

$$R_1\text{-}OH + OH^- = R_1\text{-}O + H_2O$$

$$R_1\text{-}O^- + CO_2 = R_1\text{-}O\text{-}COO^-$$

These reactions are excluded from consideration because the amount of products is negligibly small (Jensen *et al.*, 1954). Astarita *et al.* (1964) report that these reactions take place only in a basic solution where pH is 11 or greater; these reactions can be neglected as the pH of even a slightly carbonated solution is less than 10.

The chemical reactions 1 to 7 are accompanied by the vapor-liquid equilibria of the volatile species.

$$CO_2\ (l) = CO_2\ (g) \qquad \text{— (3.8)}$$

$$H_2S\ (l) = H_2S\ (g) \qquad \text{— (3.9)}$$

$$H_2O\ (l) = H_2O\ (g) \qquad \text{— (3.10)}$$

Free amine may also be present in the vapor phase. Under the conditions of interest, the vapor pressures of the amines are very small and we can assume that the amine is present only in the liquid phase. The thermodynamic framework developed in the previous chapter enables us to write down the equilibrium relations among the reacting species. These equations are as follows:

$$K_W = \gamma(H^+)\ \gamma(OH^-)\ m(H^+)\ m(OH^-) / x_W \qquad \text{— (3.11)}$$

$$K_{1C} = \gamma(H^+)\ \gamma(HS^-)\ m(H^+)\ m(HS^-) / \gamma(H_2S)\ m(H_2S) \qquad \text{— (3.12)}$$

$$K_{1Y} = \gamma(H^+)\ \gamma(HCO_3^-)\ m(H^+)\ m(HCO_3^-) / \gamma(CO_2)\ m(CO_2)\ x_W \qquad \text{— (3.13)}$$

$$K_1 = \gamma(RR'NH_2^+)\ \gamma(OH^-)\ m(RR'NH_2^+)\ m(OH^-) / \gamma(RR'NH)\ m(RR'NH)\ x_W \qquad \text{— (3.14)}$$

$$K_A = \gamma(H^+)\ \gamma(RR'NCOO^-)\ m(H^+)\ m(RR'NCOO^-) / \gamma(RR'NH)\ \gamma(CO_2)\ m(RR'NH)\ m(CO_2) \qquad \text{— (3.15)}$$

$$K_{2C} = \gamma(H^+)\ \gamma(S^=)\ m(H^+)\ m(S^=) / \gamma(HS^-)\ m(HS^-) \qquad \text{— (3.16)}$$

$$K_{2Y} = \gamma(H^+)\ \gamma(CO_3^=)\ m(H^+)\ m(CO_3^=) / \gamma(HCO_3^-)\ m(HCO_3^-) \qquad \text{— (3.17)}$$

$$\phi(CO_2)\ y(CO_2)\ P = H(CO_2)\ \gamma(CO_2)\ m(CO_2) \qquad \text{— (3.18)}$$

$$\phi(H_2S)\ y(H_2S)\ P = H(H_2S)\ \gamma(H_2S)\ m(H_2S) \qquad \text{— (3.19)}$$

$$\phi_W\ y_W\ P = (P_W)_{VP}\ x_W \qquad \text{— (3.20)}$$

The reference states have been defined in Chapter II. Equations (3.11) to (3.19) describe the rigorous thermodynamic criteria of equilibrium in the CO_2 / H_2S / amine / water system. Equation (3.20) for water is based on the assumption that $\phi_W = 1$ for pure water at its vapor pressure.

The mass balance and the electric charge balance are given by the following equations:

$$m_A = m(RR'NH) + m(RR'NH_2^+) + m(RR'NCOO^-) \qquad \text{— (3.21)}$$

$$m_A\ \alpha(CO_2) = m(CO_2) + m(HCO_3^-) + m(CO_3^=) + m(RR'NCOO^-) \qquad \text{— (3.22)}$$

$$m_A\,\alpha(H_2S) = m(H_2S) + m(HS^-) + m(S^=) \qquad \text{— (3.23)}$$

$$m(H^+) + m(RR'NH_2^+) = m(OH^-) + m(HS^-) + m(HCO_3^-) + m(RR'NCOO^-) + 2\,m(S^=) + 2\,m(CO_3^=) \qquad \text{— (3.24)}$$

Here $\alpha(CO_2)$ and $\alpha(H_2S)$ are the mole ratios in liquid (carbon to nitrogen and sulfur to nitrogen).

Olofsson and Hepler (1975) give a set of best values for the thermodynamic equilibrium constant, K_w. These values were obtained from an analysis of several experimental investigations and are consistent with other thermodynamic properties such as the standard enthalpy of ionization. They recommend the following equation for K_w, valid upto 150°C.

$$-\log_{10} K_W = 142\,613.6/T + 4229.195 \log_{10} T - 9.7384\,T + 0.012\,963\,8\,T^2 - 1.150\,68\times10^{-5}\,T^3 + 4.602\times10^{-9}T^4 - 8909.483 \qquad \text{— (3.25)}$$

Rao and Hepler (1977) have similarly analyzed the equilibrium constants and the thermodynamics of ionization of aqueous hydrogen sulfide. For temperatures between 0°C and 250°C, they recommend the following equation:

$$\log_{10} K_{1C} = -6045.2/T + 106.67 - 37.744 \log_{10} T \qquad \text{— (3.26)}$$

The first ionization constant of carbonic acid was measured by Read (1975) from 25°C to 250°C. His results can be correlated by the following equation:

$$\ln K_{1Y} = 413.7285 + 4.431\,786\times10^{-2}\,T - 67.3414 \ln T - 1.726\,204\times10^{4}/T \qquad \text{— (3.27)}$$

The most reliable measurements of the dissociation constants of the alkanolamines are those of Bates and coworkers. Bates and Pinching (1951) recommend the following equation for the acidic dissociation constant of MEA, from 0°C to 50°C.

$$-\log_{10} K_{bh} = 2677.91/T + 0.3869 + 0.000\,427\,7\,T \qquad \text{— (3.28)}$$

The basic dissociation constant, K_i can be obtained from K_{bh} and K_w by the equation:

$$K_i = K_w/K_{bh} \qquad \text{— (3.29)}$$

Bower *et al.* (1962) give the following equation for the acidic dissociation constant of DEA, from 0°C to 50°C.

$$-\log_{10} K_{bh} = 1830.15/T + 4.0302 - 0.004\,326\,1\,T \qquad \text{— (3.30)}$$

Bates and Allen (1960) report the acidic dissociation constant of TEA, from 0°C to 50°C.

$$-\log_{10} K_{bh} = 1341.16/T + 4.6252 - 0.0045666\,T \qquad \text{— (3.31)}$$

The measurements of the dissociation constant of the alkanolamines have been reported only for the temperature range of 0°C to 50°C. No measurements have been reported for DIPA, DGA and MDEA.

Jensen *et al.* (1954) studied the reactions between carbon dioxide and alkanolamines. They report the equilibrium constants for carbamate formation for MEA and DEA at 18°C. They have used the Bjerrum expression,

$$-\log_{10} \gamma = 0.3\,(c_{ion})^{0.3333}$$

to calculate the equilibrium constant. McNeil (1965) studied the same reaction, but used a different method to analyze his results. Tertiary amines do not form carbamates. No data have been reported for DIPA and DGA.

For moderate degrees of carbonation, the carbamate is the predominant product of the reaction. It is indeed unfortunate that this key reaction has received so little attention from researchers. At present, the equilibrium constants for carbamate formation are available only for MEA and DEA at temperatures of 18°C and 20°C. These measurements have been

interpreted on the basis of untested models.

The remaining two reactions, the dissociation of the bisulfide and bicarbonate ions are important only at very low loadings of the acid gases. The second ionization constant of hydrogen sulfide has been measured by Kryukov *et al.* (1974). They give the following equation for the dependence of K_{2C} on temperature, valid from 25°C to 250°C.

$$- \log_{10} K_{2C} = 2892.91/T + 4.448 - 0.002\ 514\ T \qquad \text{— (3.32)}$$

The second ionization constant for the carbonic acid has been measured by Harned and Scholes (1941), Cuta and Strafelda (1954) and Ryzhenko (1963). Their measurements, as reported by Kent and Eisenberg, may be correlated by the equation:

$$\ln K_{2Y} = 23.869\ 04 - 4.458\ 435\times10^{-2}\ T - 2.245\ 836 \ln T - 6433.628/T \qquad \text{— (3.33)}$$

The Henry's constant for carbon dioxide has been measured by Wiebe and Gaddy (1940), Zel'venskii (1937) and Ellis (1959). These data were correlated by the equation:

$$\ln H(CO_2) = - 4379.848/T + 36.725\ 75 - 2.387\ 349\times10^{-2}\ T \qquad \text{— (3.34)}$$

Lee and Mather (1978) have measured the Henry's constant for hydrogen sulfide. They have also reviewed the earlier measurements of the Henry's constant. Their data were correlated by the equation:

$$\ln H(H_2S) = - 4788.603/T + 38.4457 - 2.897\ 821\times10^{-2}\ T \qquad \text{— (3.35)}$$

1. Kent and Eisenberg Model

Van Krevelen *et al.* used the following method for calculating the vapor pressures of ammonia and hydrogen sulfide over aqueous solutions.

Instead of the thermodynamic equilibrium constant and the Henry's constant, van Krevelen *et al.* used the pseudo-equilibrium constants defined as follows:

$$K' = K\ \gamma(H_2S)\ \gamma(NH_3) / \gamma(HS^-)\ \gamma(NH_4^+) = m(HS^-)\ m(NH_4^+) / m(H_2S)\ m(NH_3) \qquad \text{— (3.36)}$$

$$H'(H_2S) = H(H_2S)\ \gamma(H_2S) / \phi(H_2S) = y(H_2S)\ P / m(H_2S) \qquad \text{— (3.37)}$$

Van Krevelen *et al.* have used molarity instead of molality as the measure of concentration. The use of molality does not, however, alter the essential features of their method. Van Krevelen *et al.* proposed equations for relating these pseudo-equilibrium constants to the ionic strength of the solution. The ionic strength is defined as:

$$\mu = 0.5\ \Sigma\ m_i\ z_i^2 \qquad \text{— (3.38)}$$

It has been claimed that the dependence of $K_1'_C$ and $H'(H_2S)$ on the ionic strength is linear. In their work, van Krevelen *et al.* have ignored the second ionization of hydrogen sulfide. They have also neglected the concentrations of the hydrogen and hydroxyl ions.

Danckwerts and McNeil used this approach to predict the equilibrium partial pressure of carbon dioxide over carbonated amine solutions. The central feature of this model is the use of pseudo-equilibrium constants and their dependence on the ionic strength. The ratio of the pseudo-equilibrium constant at a certain ionic strength to that at zero ionic strength has been termed the "ionic characterization factor". The most serious limitation of this model is that the ionic strength alone is not sufficient to determine the ionic characterization factors. Secondly, the ionic characterization factors may not be linearly related to the ionic strength. Thirdly, the dependence of these factors on the ionic strength can not be

determined without making additional simplifications. For example, several species may have to be neglected from the balance equations.

Kent and Eisenberg tried to correlate the solubility data using the published equilibrium constants without using the ionic characterization factors. They found that the predicted values deviate substantially from the experimental values. Instead of using the ionic characterization factors, they correlated the data by treating K_1 and K_A as variables. They accepted the published values of other equilibrium constants and found K_1 and K_A by fitting the data for 15.3 weight percent MEA solution and 20.5 weight percent DEA solution. The Kent and Eisenberg model is based on a set of reactions that is chemically equivalent to reactions (3.1) to (3.7). The model equations are listed below:

Reactions:

$$RR'NH_2^+ = RR'NH + H^+ \quad \text{— (3.39)}$$

$$RR'NCOO^- + H_2O = RR'NH + HCO_3^- \quad \text{— (3.40)}$$

$$H_2O + CO_2 = H^+ + HCO_3^- \quad \text{— (3.41)}$$

$$H_2O = H^+ + OH^- \quad \text{— (3.42)}$$

$$HCO_3^- = H^+ + CO_3^= \quad \text{— (3.43)}$$

$$H_2S = H^+ + HS^- \quad \text{— (3.44)}$$

$$HS^- = H^+ + S^= \quad \text{— (3.45)}$$

$$CO_2\ (l) = CO_2\ (g) \quad \text{— (3.46)}$$

$$H_2S\ (l) = H_2S\ (g) \quad \text{— (3.47)}$$

Equilibrium relations:

$$K_1 = [H^+]\,[RR'NH] / [RR'NH_2^+] \quad \text{— (3.48)}$$

$$K_2 = [RR'NH]\,[HCO_3^-] / [RR'NCOO^-]\,[H_2O] \quad \text{— (3.49)}$$

$$K_3 = [H^+]\,[HCO_3^-] / [CO_2]\,[H_2O] \quad \text{— (3.50)}$$

$$K_4 = [H^+]\,[OH^-] / [H_2O] \quad \text{— (3.51)}$$

$$K_5 = [H^+]\,[CO_3^=] / [HCO_3^-] \quad \text{— (3.52)}$$

$$K_6 = [H^+]\,[HS^-] / [H_2S] \quad \text{— (3.53)}$$

$$K_7 = [H^+]\,[S^=] / [HS^-] \quad \text{— (3.54)}$$

$$H(CO_2) = P(CO_2) / [CO_2] \quad \text{— (3.55)}$$

$$H(H_2S) = P(H_2S) / [H_2S] \quad \text{— (3.56)}$$

Balance equations:

$$[H^+] + [RR'NH_2^+] = [OH^-] + [RR'NCOO^-] + [HCO_3^-] + [HS^-] + 2\,[CO_3^=] + 2\,[S^=] \quad \text{— (3.57)}$$

$$c_A = [RR'NH] + [RR'NH_2^+] + [RR'NCOO^-] \quad \text{— (3.58)}$$

$$c_A\,\alpha(CO_2) = [CO_2] + [HCO_3^-] + [RR'NCOO^-] + [CO_3^=] \quad \text{— (3.59)}$$

$$c_A\,\alpha(H_2S) = [H_2S] + [HS^-] + [S^=] \quad \text{— (3.60)}$$

In these equations, the quantities in the square brackets are the molarities of various species, with the exception of $[H_2O]$, which is the mole fraction of water.

It would be incorrect to use equations like (3.50) with K_3 obtained from literature. The activity coefficients even in moderately charged solutions are of the order of 0.5. The ratio of concentrations in such solution would be four times the ratio given by Equation (3.50). It is clear that even if the Kent and Eisenberg model succeeds in predicting the correct partial pressures, it would fail to predict the concentrations of the ionic species.

The VLE relations are similarly inaccurate as they do not include the fugacity coefficients. If the acid gas partial pressure is a few MPa, the fugacity coefficient may be far from unity.

To improve the predictions made by this method, Kent and Eisenberg treated K_1 and K_2 as adjustable parameters and determined them by fitting the model to experimental data. They were able to obtain excellent fits by using this approach. They also discovered that the constants K_1 and K_2 obtained in this manner show an Arrhenius dependence on temperature.

Kent and Eisenberg obtained their constants by fitting the data for 2.5 N MEA solutions. Nasir used these constants to predict the acid gas partial pressures over 5.0 N MEA solutions. He found that the errors in partial pressures are often in excess of 100 percent. The Kent and Eisenberg model was also unable to predict the partial pressures accurately when the acid gas loadings were were either very low or very high.

This procedure of lumping all non-idealities into two adjustable parameters is unsatisfactory for many reasons. The thermodynamic rigor is lost if the experimentally measured values are disregarded. The constants K_1 and K_2 depend on the normality of amine solution. The predictions are accurate only in a narrow range of loadings (0.2 to 0.7). The constants K_1 and K_2 are obtained by fitting the pure component data; i.e. the data for one acid gas and amine solution. When these constants are used to predict the partial pressures with both acid gases present, the predictions are highly inaccurate. The attractive feature of this model is that the model equations are amenable to algebraic manipulations, thus permitting hand-calculation of the equilibria.

2. Klyamer *et al.* Model

Atwood et al. proposed a method of calculation of equilibria in the H_2S / amine / water system. Their scheme was used by Klyamer and Kolesnikova (1972) to predict the equilibria in the CO_2 / amine / water system. Klyamer *et al.* generalized the scheme to make it applicable to the CO_2 / H_2S / amine / water system. The central feature of this model is the use of "mean ionic activity coefficient". The activity coefficients of all ionic species are assumed to be equal.

This assumption has some basis in theory. In the case of a uni-univalent electrolyte, the assumption is certainly a valid one. Consider the reaction:

$$MX = M^+ + X^- \qquad \text{— (3.61)}$$

Here the individual activity coefficients $\gamma(M^+)$ and $\gamma(X^-)$ (usually written as γ_+ and γ_-) are not measurable properties. By virtue of the charge balance, concentrations of the anion and the cation are equal to each other and can not be varied independently. This means that γ_+ and γ_- are experimentally inaccessible. Only the product $\gamma_+\gamma_-$ can be measured. For a uni-univalent electrolyte, the mean ionic activity coefficient is defined by

$$\gamma = (\gamma_+\gamma_-)^{0.5} \qquad \text{— (3.62)}$$

The quantity γ is measurable and is sufficient to characterize the equilibria. For a single electrolyte, the assumption of equal activity coefficients is tautologous. For a mixture of electrolytes, the Debye-Huckel theory gives an expression for the activity coefficients. The

Debye-Huckel theory is applicable only at low ionic strengths. The electrolyte solution is assumed to be a collection of electric charges embedded in a dielectric medium. The resulting expression,

$$ln\ \gamma_i = -\ A\ z_i^2\ \mu^{0.5} \qquad \text{— (3.63)}$$

shows that the ionic coefficients are equal in a dilute solution of uni-univalent electrolytes.

However, there is no reason to believe that the ionic activity coefficients will be equal in a solution of high ionic strength. The assumption is still good if only one anion and one cation are present in significant amount. This is generally *not* the case for the CO_2 / H_2S / amine / water system.

The Klyamer *et al.* model is also based on a set of reactions that is chemically equivalent to the reactions 1 to 7. These reactions are not the same as those used by Kent and Eisenberg, but are chemically equivalent. The model equations are presented below.

Reactions:

$$RR'NH + H_2O = RR'NH_2^+ + OH^- \qquad \text{— (3.64)}$$

$$H_2S = H^+ + HS^- \qquad \text{— (3.65)}$$

$$H_2O = H^+ + OH^- \qquad \text{— (3.66)}$$

$$HS^- = H^+ + S^= \qquad \text{— (3.67)}$$

$$2\ RR'NH + CO_2 = RR'NH_2^+ + RR'NCOO^- \qquad \text{— (3.68)}$$

$$H_2O + CO_2 = H^+ + HCO_3^- \qquad \text{— (3.69)}$$

$$HCO_3^- = H^+ + CO_3^= \qquad \text{— (3.70)}$$

Equilibrium relations:

$$K_i = \gamma^2\ m(RR'NH_2^+)\ m(OH^-) / a\ \alpha^2\ m(RR'NH) \qquad \text{— (3.71)}$$

$$K_W = \gamma^2\ m(H^+)\ m(OH^-) / \alpha \qquad \text{— (3.72)}$$

$$K_{1C} = \gamma^2\ m(H^+)\ m(HS^-) / m(H_2S) \qquad \text{— (3.73)}$$

$$K_{2C} = \gamma\ m(H^+)\ m(S^=) / m(HS^-) \qquad \text{— (3.74)}$$

$$H'(H_2S) = m(H_2S) / p(H_2S) \qquad \text{— (3.75)}$$

$$K_M = \gamma^2\ m(RR'NH_2^+)\ m(RR'NCOO^-) / a^2\ \alpha^2\ m^2(RR'NH)\ p(CO_2) \qquad \text{— (3.76)}$$

$$K_{1Y} = \gamma^2\ m(H^+)\ m(HCO_3^-) / \alpha\ m(CO_2) \qquad \text{— (3.77)}$$

$$K_{2Y} = \gamma\ m(H^+)\ m(CO_3^=) / m(HCO_3^-) \qquad \text{— (3.78)}$$

$$H'(CO_2) = m(CO_2) / p(CO_2) \qquad \text{— (3.79)}$$

The balance equations are identical to Equations (3.21) to (3.24). In these equations, γ is the mean ionic activity coefficient, α is the mole fraction of water and ($a\alpha$) is the activity coefficient of the free amine. $H'(H_2S)$ and $H'(CO_2)$ are the inverted Henry's constants. The mean ionic activity coefficient is determined from a plot given by Atwood *et al.* where it is related to the ionic strength of the solution. This plot was obtained by fitting the data for H_2S / amine / water system and smoothing. Klyamer *et al.* assume that the relation between the mean ionic activity coefficient and the ionic strength is the same in the CO_2 / H_2S / amine / water system. The ratio "a" is related to the molality of of free alkanolamine. This functional relation was estimated by Atwood *et al.* from the data of Sivertz *et al.* (1940).

The Klyamer *et al.* model also assumes that the activity coefficients of the free H_2S and free CO_2 are equal to unity. The fugacity coefficients are also assumed to be equal to unity.

The equality of activity coefficients makes this model suitable for analytical solution.

Simple expressions for the partial pressures may be derived from these equations. These expressions have been derived in Appendix A.

The Klyamer *et al.* model, with $\gamma = 1$ and $a\alpha = 1$, is algebraically equivalent to the Kent and Eisenberg model. If these substitutions are made in the expressions for the Klyamer *et al.* model, the corresponding expressions for the Kent and Eisenberg model are obtained.

Nasir made two improvements in the Klyamer *et al.* model. He incorporated into the model the fugacity coefficients based on the Redlich-Kwong equation of state. He made γ, the mean ionic activity coefficient a function of the initial amine concentration and the temperature. These changes resulted in some improvement in accuracy, especially at high pressures.

3. Proposed Model

The main problem in the calculation of VLE in multicomponent systems is the estimation of the fugacity coefficients and the activity coefficients. Kent and Eisenberg avoid this problem by lumping all non-idealities into two adjustable parameters. Klyamer *et al.* assumed that all ionic activity coefficients are equal and that these can be estimated from an empirical correlation. The failure of both models indicates the need for a better method to estimate the activity coefficients and especially at high pressures, the fugacity coefficients have to be estimated accurately. The fugacity coefficients are related to the volumetric behavior of the vapor phase.

$$\ln \phi_i = \int (Z_i - 1) \, d \ln P \qquad \text{— (3.80)}$$

Here $Z_i = Pv_i/RT$ and v_i = the partial molar volume of the i-th component. We estimate the fugacity coefficients using the Peng-Robinson equation of state. This equation has proved to be superior to the original R-K equation and the Soave modification of the R-K equation. The Peng-Robinson equation is of the form

$$P = (RT/(v-b)) - a(T)/(v(v+b) + b(v-b)) \qquad \text{— (3.81)}$$

The fugacity coefficient of component i can be calculated from the following equation:

$$\ln \phi_i = (b_i/b)(Z-1) - \ln (Z-B) \, (1/\sqrt{8})(A/B)\times$$
$$((2 \Sigma y_i a_{ij}/a)-b_i/b) \ln ((Z+2.414 B)/(Z-0.414 B)) \qquad \text{— (3.82)}$$

where

$$A = aP/R^2T^2, \; B = bP/RT, \; Z = Pv/RT, \; a = \Sigma y_i y_j a_{ij}, \; b = \Sigma y_j b_j \text{ and } a_{ij} = (1-\delta_{ij})(a_i a_j)^{0.5} \qquad \text{— (3.83)}$$

In Equation (3.83), δ_{ij} is an empirically determined binary interaction coefficient. This coefficient is independent of temperature except for water-containing systems.

The constants a_j and b_j are related to the critical properties and the acentric factor of the component j. The subscript j has been omitted in the following equations for convenience.

$$a(T) = a(T_C)\cdot\alpha(T_r, \omega)$$
$$b(T) = b(T_C)$$
$$a(T_C) = 0.45724 \, R^2 \, (T_C)^2 \, / \, P_C$$
$$b(T_C) = 0.07780 \, R \, T_C \, / \, P_C$$

$$\alpha^{0.5}(T_r, \omega) = 1 + \kappa[1 - (T_r)^{0.5}]$$

$$\kappa = 0.37464 + 1.54226\ \omega - 0.26992\ \omega^2 \qquad \text{— (3.84)}$$

The compressibility factor Z is determined by solving Equation (3.81). The equation yields one or three real roots depending upon the number of phases in the system. In the two-phase region, the largest root is the compressibility factor of vapor. The constants required for solving Equation (3.81) are easily determined from Equations (3.83) and (3.84). The Peng-Robinson equation is a cubic equation and it can be solved analytically. The predictions made by the P-R equation are particularly good in the critical region. This is advantageous as the critical temperatures of CO_2 and H_2S fall in the range of interest.

The Debye-Huckel expression may be used for the prediction of activity coefficients in very dilute solutions. For more concentrated solutions, Guggenheim (1935) gives the extended Debye-Huckel expression

$$ln\ \gamma_k = -\ A\ (z_k)^2\ \mu^{0.5}\ /\ (1 + b_k\ \mu^{0.5}) + 2\ \Sigma\ \beta_{kj}\ m_j \qquad \text{— (3.85)}$$

The first term expresses the Debye-Huckel law and represents the electrostatic forces. The second term takes into account the short range van der Waals forces. The quantity A is related to the dielectric constant of the solvent. Usually b_k may be considered a constant. Values of 1.0, 1.2 or 1.5 are commonly found in the literature.

In Equation (3.85), β_{kj} have been considered constants. Scatchard (1936) has shown that β_{kj} is a slowly varying function of the ionic strength. The interaction parameters may also depend upon the temperature of the system. However, Edwards *et al.* found this effect to be small.

Pitzer (1973) has derived a more accurate expression for the activity coefficients. His expression is much too complicated to be used for alkanolamine solutions. The available information on the reactions of the alkanolamines is insufficient to determine the specific interaction parameters in the Pitzer's expression. Beutier and Renon (1978) have used Pitzer's expression to calculate the VLE in NH_3-CO_2-H_2O, NH_3-H_2S-H_2O and NH_3-SO_2-H_2O systems. Though the reactions occurring in these systems are well-studied, Beutier and Renon had to make several assumptions about the interaction parameters to make the expression manageable. The extended Debye-Huckel expression seems to be the appropriate one for the CO_2 / H_2S / amine / water system. Given the complexity of this expression, a good computer program for solving the VLE equations becomes a necessity.

IV. METHOD OF SOLUTION

The problem of correlating the VLE data consists of (1) the interpretation of the data to obtain the required parameters and (2) the application of the knowledge thus obtained to predict the equilibria. In both stages, one needs a numerical method to relate the vapor and the liquid compositions.

The mathematical problem is to solve Equations (3.11) to (3.24). The fugacity coefficients in these equations are obtained from the Peng-Robinson equation of state. The activity coefficients are obtained from the extended Debye-Huckel theory of electrolyte solutions. Essentially one has to solve a system of nonlinear algebraic equations.

The sequence of calculations is as follows: (1) The temperature, the normality of amine and either the acid gas partial pressures or the mole ratios in liquid are specified. (2) The equilibrium constants, the Henry's constants, the dielectric constant of water and the binary interaction parameters are calculated. (3) A preliminary solution is calculated by setting all activity coefficients and the fugacity coefficients equal to unity. (4) The preliminary estimate is refined using Brown's method for solving a system of nonlinear equations. (5) The equilibrium composition is determined from the converged solution.

A FORTRAN program for calculating the equilibrium composition is presented in Appendix C. Brown's method used in this program is based on a partial pivoting technique similar to Gaussian elimination. The method is at least second order convergent, requires fewer function evaluations as compared to the Newton's method and is derivative-free. This method is especially attractive when the number of variables is large or when the equations to be solved are complicated. Brown's method is described in Appendix B.

To obtain a fast convergence with Brown's method, the variables and the functions have to be "normalized". The variables are normalized if they are all of the same order of magnitude. The molalities and the partial pressures in the CO_2 / H_2S / amine / water system range over several orders of magnitude. Molalities as low as 10^{-10} mol/kg-water and pressures as high as 10^6 Pa are common. To normalize these variables, the equations were formulated in terms of their logarithms. For example, instead of $p(CO_2)$, $ln\ p(CO_2)$ was treated as a variable. Even though the original variables range over several orders of magnitudes, their logarithms are of the same order of magnitude. When the logarithms are treated as variables, the partial derivatives in the Jacobian matrix are calculated with respect to the logarithms. Instead of the original problem, $\mathbf{f(x)} = 0$, we solve the problem $\mathbf{g(y)} = 0$; where $y_i = ln\ x_i$. The use of logarithms has an additional advantage that the solution remains feasible at each step. Regardless of the magnitude and the sign of y_i, x_i always remains positive.

The functions are normalized if the convergence criterion can be correctly expressed as

$$|\mathbf{f(x)}| < \epsilon$$

where ϵ is a reasonably small positive constant. For example, consider the function

$f(x_1, x_2) = x_1 - x_2$

and the error criterion

$|f(x_1, x_2)| < 10^{-3}$.

If $x_1 = 100\ 000$ and $x_2 = 99\ 999$, the error criterion is not satisfied even though x_1 and x_2 agree to four digits. On the other hand, if $x_1 = 10^{-15}$ and $x_2 = 10^{-20}$, the error criterion is satisfied even though x_1 is 100 000 times as large as than x_2. This means that the function $f(x_1, x_2)$ is not normalized. A better way to write this function would be

$g(x_1, x_2) = 1 - x_1/x_2$

In this case, the error criterion would be meaningful for any x_1 and x_2.

Equations (3.11) to (3.24) may be normalized as follows:

$f_1 = 1 - \gamma(H^+)\ \gamma(OH^-)\ m(H^+)\ m(OH^-) / K_w\ x_w$

$f_2 = 1 - \phi(CO_2)\ y(CO_2)\ P/H(CO_2)\ \gamma(CO_2)\ m(CO_2)$

$f_3 = 1 - (\ m(H_2S) + m(HS^-) + m(S^=)\ ) / \alpha(H_2S)\ m_A$

$f_4 = 1 - \Sigma$ (negative charges) / Σ (positive charges)

The remaining equations may be normalized in the same way.

After the variables and the functions are thus normalized, the programming is generally straightforward, unless one or more components are absent. For example, if no hydrogen sulfide is present in the system, $m(H_2S)$, $m(HS^-)$ and $m(S^=)$ are all equal to zero. As *ln* 0 is undefined, the method described above has to be modified to handle these cases. This is done by using two arrays, I_V and I_E. These arrays are defined as follows:

The array I_V contains the *indices* of the variables to be determined. When a variable is known to be zero, its index is not included in I_V. If $x_2 = 0$, $I_V = [1, 3, 4, \ldots]$. Similarly, the array I_E contains the indices of the equations to be solved. These arrays can be calculated if the species present in the system are known. If all components are present in the system, $I_V(i) = I_E(i) = i$.

If some components are absent from the system, a smaller set of equations is solved. The equations solved are:

$f_k(\mathbf{x}) = 0$ $\qquad k = I_E(1), I_E(2), \ldots$

These equations are solved in terms of the variables x_j where

$j = I_V(1), I_V(2), \ldots$

Using this technique, we avoid taking logarithms of quantities which are zero, while normalizing the non-zero variables.

The indexing also permits us to use the same program to calculate the partial pressures when the loadings are known and to calculate the loadings when the partial pressures are known. If the partial pressure of CO_2 is known, the index of the variable denoting $p(CO_2)$ is not included in I_V. At the same time, the index of the variable denoting $\alpha(CO_2)$ is included in I_V. This has the effect of treating $\alpha(CO_2)$ as an unknown and $p(CO_2)$ as a known variable. When $\alpha(CO_2)$ is known and $p(CO_2)$ is unknown, the index of $\alpha(CO_2)$ is excluded from I_V and that of $p(CO_2)$ is included in I_V.

In summary, the computer program has the following features:

1. The algorithm is fast and efficient.
2. The program is able to calculate the partial pressures if the mole ratios in the liquid phase are known and vice versa.

3. Although the variables are normalized by taking logarithms, the program can handle variables which are zero. Redundant equations are also avoided.

If another method is to be used to calculate the fugacity coefficients and the activity coefficients, the program can be easily modified. Only the routines that calculate these coefficients have to be rewritten.

With this program, we can predict the vapor-liquid equuilibria if the equilibrium constants, the Henry's constants and the interaction parameters are known. There are no *a priori* methods to determine the specific interaction parameters. These parameters have to be deduced from the experimental data.

The specific interaction parameters show a weak dependence on the ionic strength (Scatchard, 1936) and the temperature (Edwards *et al.*, 1975). We assume these parameters to be independent of the temperature and the ionic strength.

The specific interaction parameters represent the short range interactions (van der Waals forces). In moderately charged solutions, the similarly charged ions do not come close enough for the van der Waals forces to become important. This is called the Brønsted principle (Brønsted, 1922 and 1923). If i and j are similarly charged (both positive or both negative) ions, the Brønsted principle implies that $\beta_{ij} = 0$.

The interaction parameters may be divided into three groups: (1) the molecule-molecule interaction parameters, (2) the molecule-ion interaction parameters and (3) the ion-ion interaction parameters.

Edwards *et al.* have determined β_{aa}, the molecule-molecule interaction parameters by fitting Equation (2.85) to single-solute systems. As $\mu \rightarrow 0$,

$$ln\ \gamma_a = 2\ \beta_{aa}\ m_a$$

Thus $(2\ \beta_{aa})$ is the limiting slope of the plot of $ln\ \gamma_a$ against m_a. However, as the concentration of the solute tends to zero, the degree of dissociation tends to infinity. At zero ionic strength, the electrolyte will be fully dissociated. Edwards *et al.* assumed that the molecule-ion interaction parameters in the single solute systems are equal to zero. Without this assumption, β_{aa} can not be determined by Edwards' procedure. The molecule-molecule interaction parameters for CO_2, H_2S and RR'NH can be determined from the data of Houghton *et al.* (1957), Clarke and Glew (1970) and Sivertz *et al.* (1940). The molecule-molecule interaction parameters between the unlike species may be estimated from the combination rule proposed by Edwards *et al.*:

$$\beta_{ab} = 0.5\ (\ \beta_a + \beta_b\ )$$

As no data are available for DIPA, DGA and MDEA, it is proposed that

$$\beta_{aa}(\text{DGA}) = \beta_{aa}(\text{MEA})$$

$$\beta_{aa}(\text{DIPA}) = \beta_{aa}(\text{DEA})$$

$$\beta_{aa}(\text{MDEA}) = \beta_{aa}(\text{TEA})$$

Bromley (1972) has formulated a procedure for estimating the binary ion-ion interaction parameters. He postulated that the interaction parameter β_{ij} may be expressed as a sum of individual ion contributions, β_i and β_j.

$$\beta_{ij} = \beta_i + \beta_j$$

Further, Bromley observed a correlation between β_i and the standard partial molar entropy of the ion, $z_i S_i^0$, at 25°C. If the standard entropy of the ions are known, β_i and β_{ij} may be

estimated from Bromley's plot.

The procedure works well for CO_2 / H_2O and H_2S / H_2O systems. The entropies of ethanolammonium and the carbamate ions have not been measured. Bromley's procedure can not be applied for these ions. Bromley (1973) has also proposed a more accurate method for estimating the ion-ion interaction parameters. In addition to standard entropies, this method requires the knowledge of the proton affinities of the ions.

Beutier and Renon have found out that a unique correlation between β_i and $z_i S_i^0$ does not exist for all ions in solution. They observed different correlations for cations, halogenide ions, oxygenated polyatomic ions and proton acceptors. Even if the entropies of the ethanolammonium and the carbamate ions could be estimated, Bromley's plot could not be used with confidence.

The molecule-ion (or salting-out) parameters may also be correlated in this way. Edwards *et al.* assumed that β_{mi} depends linearly on β_i or $z_i S_i^0$. Long and McDevit (1952) have measured the salting-out parameters for carbon dioxide and hydrogen sulfide. Their data can be used to construct a plot of β_{mi} against $z_i S_i^0$. This method can be used for carbon dioxide / hydrogen sulfide / water system. The salting-out parameters for amine-containing systems have not been measured. These parameters have to be obtained from least-squares fitting of the experimental data.

Let $\mathbf{B} = [\beta_1, \beta_2, \ldots, \beta_N]$ be the array of the interaction parameters and $\mathbf{E} = [e_1, e_2, \ldots, e_M]$ be the array of the errors in predictions. We wish to find the interaction parameters $\mathbf{B}^*$ that minimize $s = |\mathbf{E}|^2$. When s is minimum,

$$\partial s / \partial \beta_i = 0, \qquad i = 1, 2, \ldots, N$$

These N equations can, in principle, be solved for the N unknown β's. However, such a procedure is not feasible because of the excessive computational effort involved. To simplify the calculations, the following assumptions may be made.

1. The interaction parameters for the species which are present in very small concentrations can be neglected.
1. The effect of the β's on the errors in prediction is assumed to be additive.

When a certain chemical species is present in a very small concentration, it has little effect on the equilibria. The concentration of that species may be neglected from the balance equations. A reduced set of equations can be solved in terms of a smaller set of variables. For example, if $S^=$ is present in a very small amount, its concentration can be ignored from the charge balance and the sulfur balance equations. The equations (except the equilibrium relation for the dissociation of the bisulfide ion) can be solved for the variables (excluding $S^=$). Secondly, the term $\beta_{ij} m_j$ in the extended Debye-Huckel theory may be neglected if m_j is small.

The additivity assumption implies that the total deviation in predictions may be expressed as a sum of the individual deviations due to each of the interaction parameters. Let $\mathbf{P}^0$ be the predictions using $\mathbf{B} = [0, 0, \ldots, 0]$ and let $\mathbf{P}$ be the measured values. Therefore, $\mathbf{E}^0 = \mathbf{P} - \mathbf{P}^0$ is the total error. The effect of the interaction parameters can be found by setting j-th parameter to a small number, say $\Delta\beta_j$. Let the new predictions be $\mathbf{P}(\Delta\beta_j)$. This means that setting the j-th parameter to $\Delta\beta_j$ has caused a deviation of $[\mathbf{P}(\Delta\beta_j)-\mathbf{P}^0]$ in the predictions. If β's are small, this deviation is proportional to the magnitude of β; i.e.

$$[\mathbf{P}(\beta_j) - \mathbf{P}^0] / \beta_j = [\mathbf{P}(\Delta\beta_j) - \mathbf{P}^0] / \Delta\beta_j$$

$$P(\beta_j) - P^0 = (\beta_j / \Delta\beta_j) [P(\Delta\beta_j) - P^0]$$

Define $C_j = [P(\Delta\beta_j) - P^0]/\Delta\beta_j$. Since the total deviation is the sum of the individual deviations,

$$C_T = \Sigma \beta_j C_j$$

This can be written as

$$C_T = X \cdot B$$

where $X = [C_1, C_2, \ldots, C_N]$. We wish to find B so that C_T is the best estimate to E^0, i.e. we wish to minimize the squared error $q = |E^0 - C_T|^2$.

$$q = (E^0 - C_T)'(E^0 - C_T)$$

Substituting $C_T = X \cdot B$ and expanding,

$$q = E^{0\prime}E^0 - B'X'E^0 - E^{0\prime}XB + B'X'XB$$

$$\partial q/\partial\beta_i = -2\ 1'X'E^0 + 2\ 1'X'XB$$

When q is minimum, $\partial q/\partial\beta_i = 0$.

$$\therefore X'XB = X'E^0$$

$$B = (X'X)^{-1}X'E^0$$

All arrays required in this method can be calculated by using the the computer program described above. The method can be extended to determine the equilibrium constants outside their range of measurement. Define $K = K_0 \exp \epsilon$. The exponential function is used to ensure that K is always positive. Given an initial estimate of K, ϵ can be determined by the least squares fitting as described above.

This method was used to correlate the equilibrium solubility of carbon dioxide, hydrogen sulfide and their mixtures in MEA, DEA and DIPA solutions. The results are presented in the next chapter.

V. RESULTS AND DISCUSSION

The procedure described in Chapter IV was applied to the CO_2 / H_2S / amine / water system. The temperature, amine normality and the acid gas loadings were provided as the input to the computer program and the predicted partial pressures were compared to the experimental data. The error in predictions was taken to be $ln\ P_{obs} - ln\ P_{pred}$. The interaction parameters were determined by minimizing the sum of the squared errors.

In Brown's method, the iterations were stopped when two successive estimates of the solution agreed to within eight significant digits or when all functions were less than 10^{-15} in absolute value. These criteria appear to be unnecessarily stringent at first sight. Brown's method possesses second order convergence properties, i.e. the number of significant digits approximately doubles in each step if the estimate is close enough to the solution. If it takes five iterations to obtain a solution correct to two significant places, it will take just two more iterations to obtain an estimate correct to eight significant places. Thus the extra effort required to increase the number of significant digits is quite small. Secondly, making the error criterion so stringent ensures that no errors are introduced by the numerical method itself.

In the CO_2 / H_2S / amine / water system, the only species which are present in significant concentration are the free amine and the ethanolammonium, carbamate, bicarbonate and bisulfide ions. This means that the interaction parameters for the other species (CO_2, H_2S, OH^-, H^+, $S^=$ and $CO_3^=$) will have little effect on the observed equilibria. At very high loadings, the concentrations of the free CO_2 and H_2S are also high.

The important interaction parameters are β(RR′NH-RR′NH), β(RR′NH-RR′NCOO$^-$), β(RR′NH-HCO$_3^-$), β(RR′NH-HS$^-$), β(RR′NH$_2^+$-RR′NCOO$^-$), β(RR′NH$_2^+$-HCO$_3^-$) and β(RR′NH$_2^+$-HS$^-$). The first of these can be determined from the correlation of Atwood *et al.*. It should be noted that there are no mixture parameters in this list. The parameters for the CO_2 / amine / water system and the H_2S / amine / water system are sufficient to predict the the equilibria in the CO_2 / H_2S / amine / water system. The required parameters may be obtained either from the single solute data or the mixture data. More computations are required if the mixture data are used to calculate the parameters.

1. Solubility of acid gases in MEA solutions

The partial pressures of H_2S over 2.5 *N* and 5.0 *N* MEA solutions at 25, 40, 60, 80, 100 and 120°C have been reported by Lee *et al.*, 1976a. Their data were used to determine β(RR′NH-HS$^-$), β(RR′NH$_2^+$-HS$^-$) and the equilibrium constant for the dissociation of MEA at 100°C. Figures 2 and 3 show comparisons between the predictions and the experimental data. The agreement is good for both 2.5 *N* and 5.0 *N* MEA solutions and at all temperatures.

Lee *et al.*, 1976b have measured the solubility of CO_2 in 1.0, 2.5, 3.75 and 5.0 *N* MEA solutions at 25, 40, 60, 80, 100 and 120°C. The equilibrium constant for the carbamate

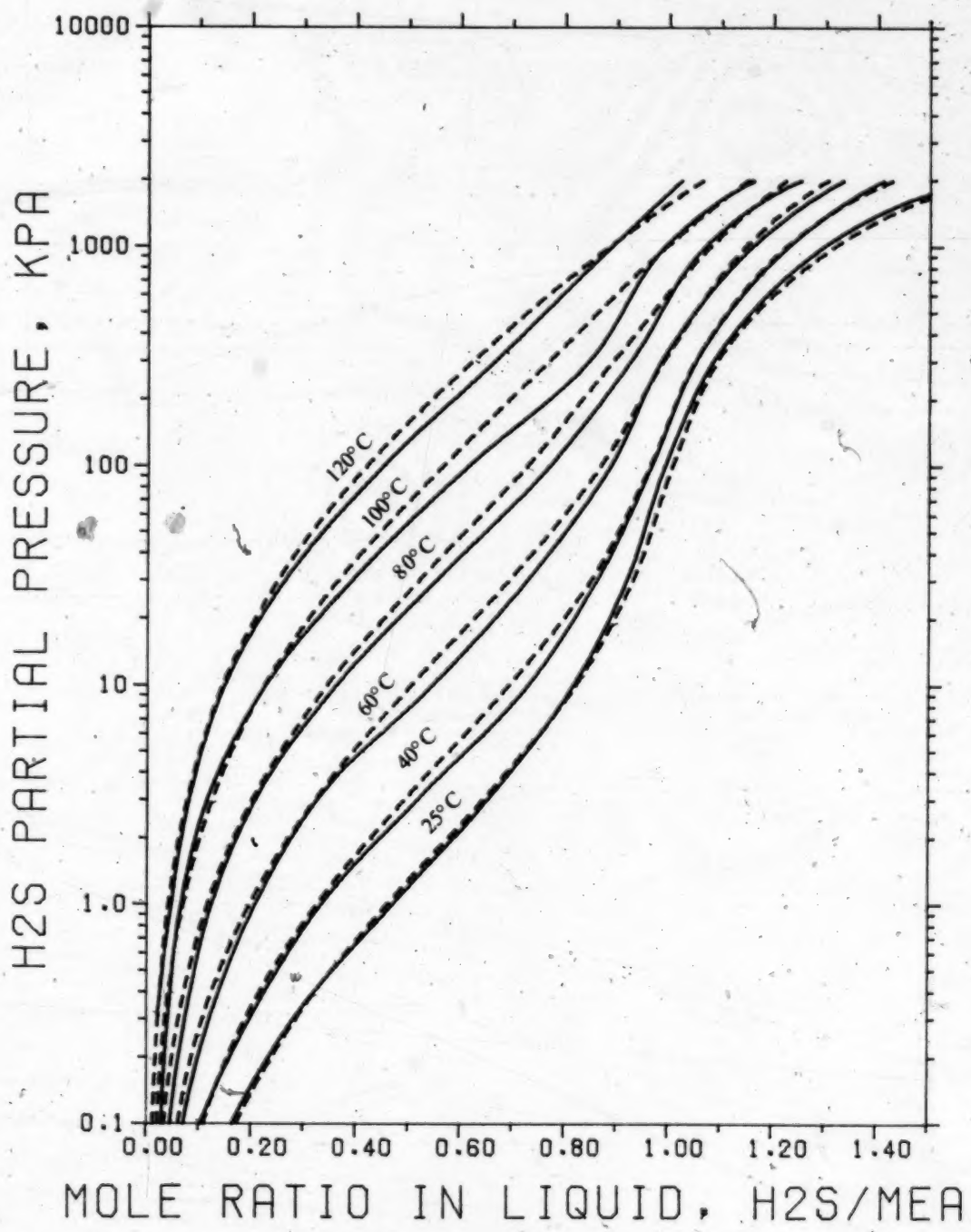

Figure 2.

SOLUBILITY OF H2S IN 2.5 N MEA SOLUTIONS

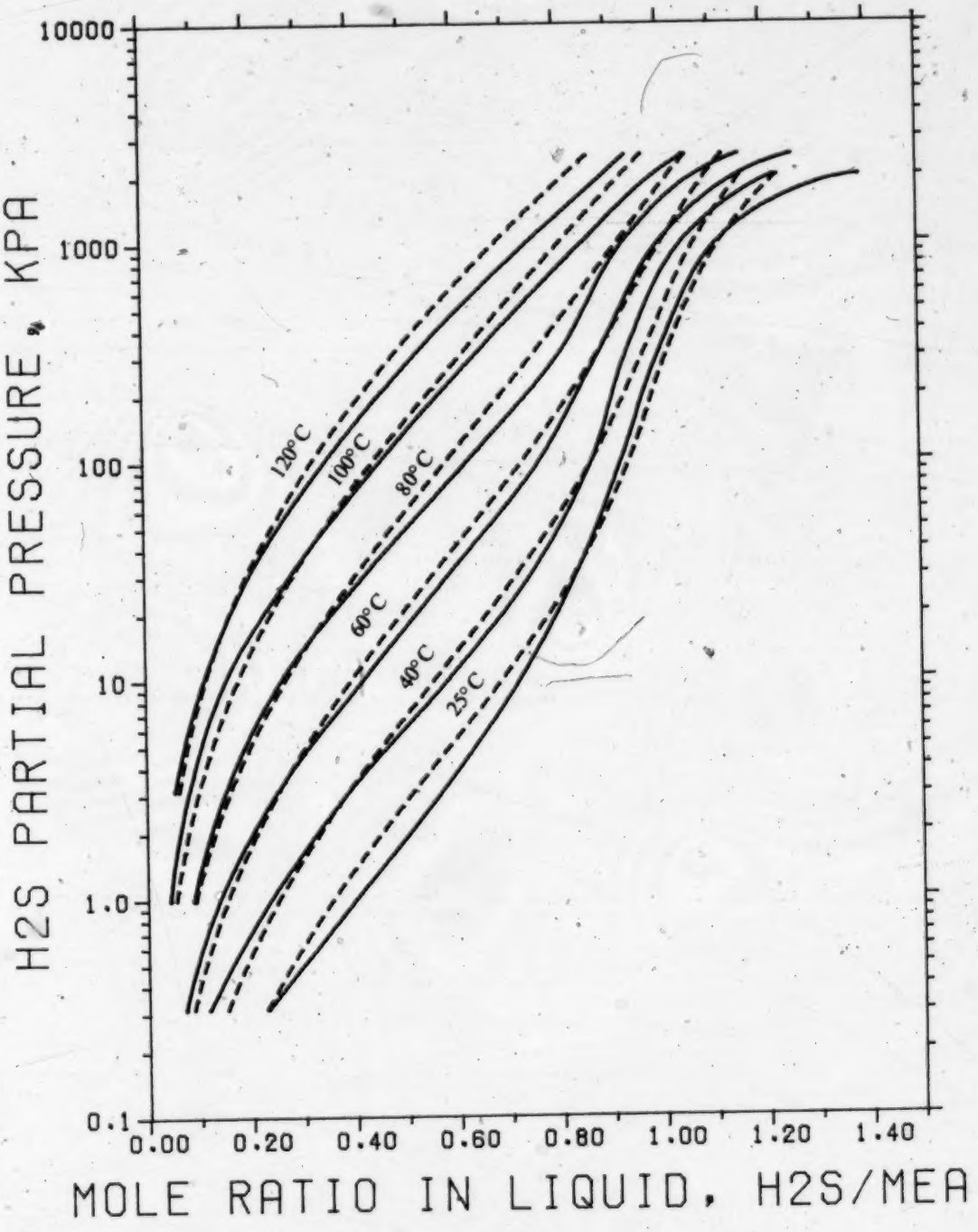

Figure 3.

SOLUBILITY OF H2S IN 5.0 N MEA SOLUTIONS

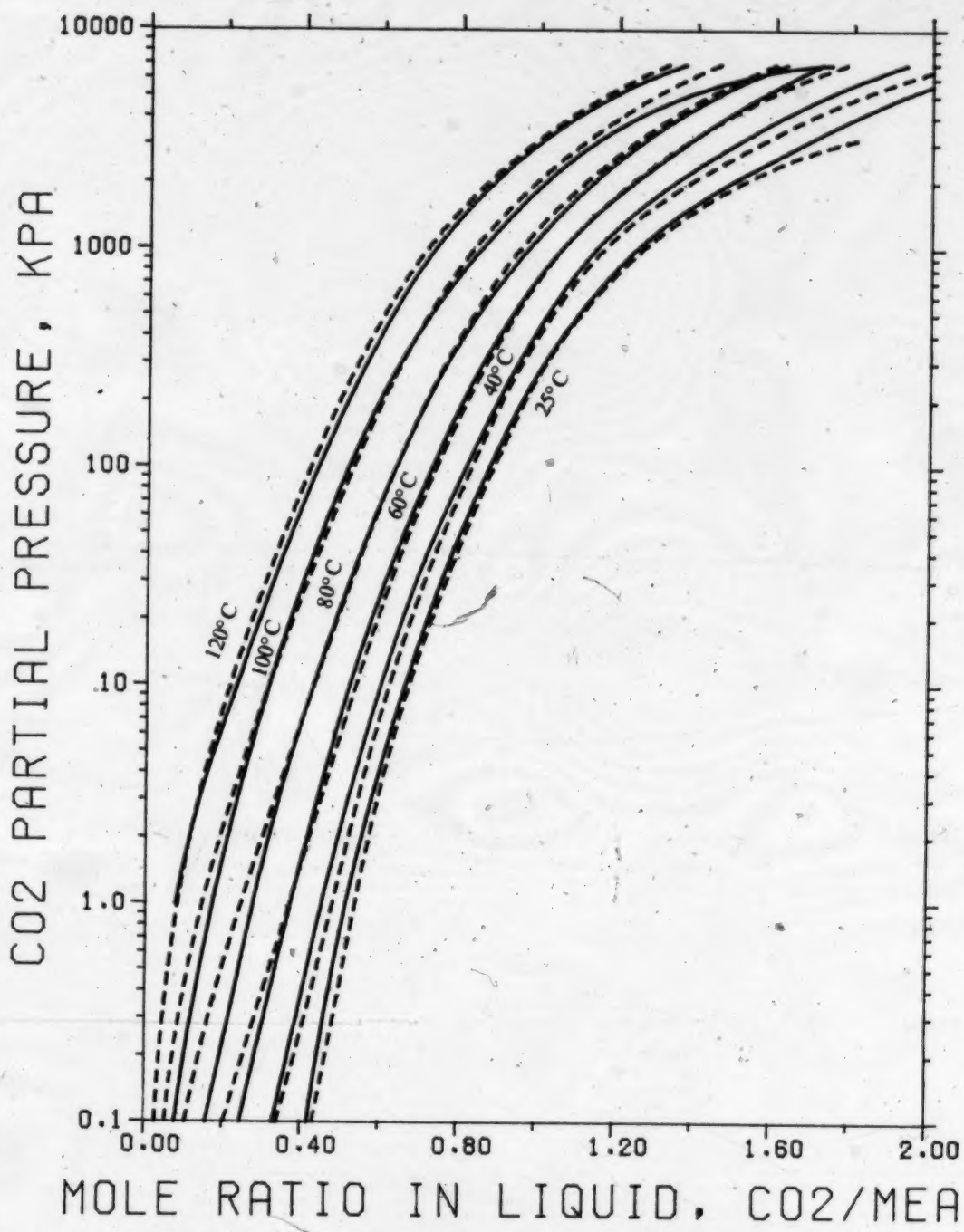

Figure 4.

SOLUBILITY OF CO2 IN 1.0 N MEA SOLUTIONS

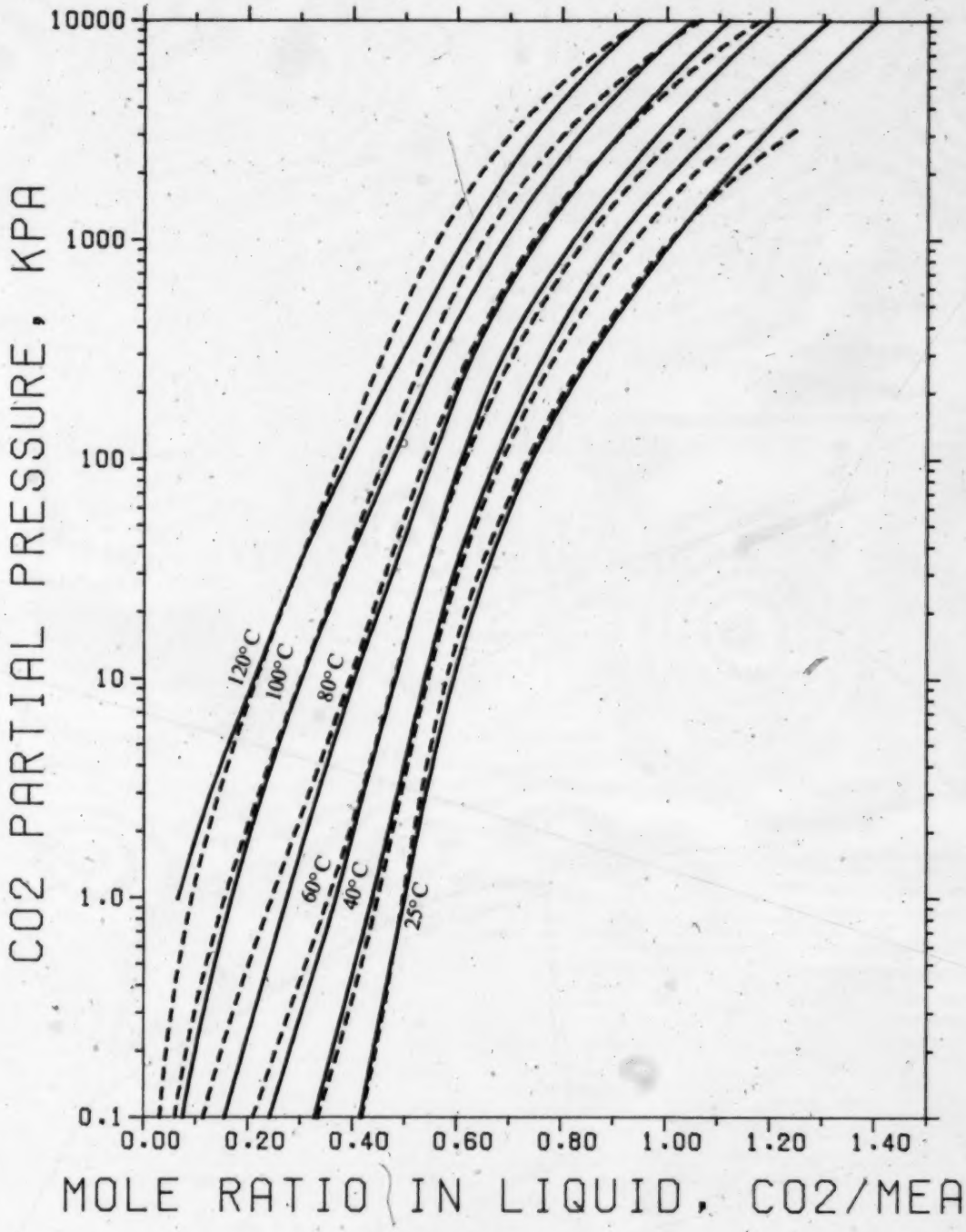

Figure 5.

SOLUBILITY OF CO2 IN 2.5 N MEA SOLUTIONS

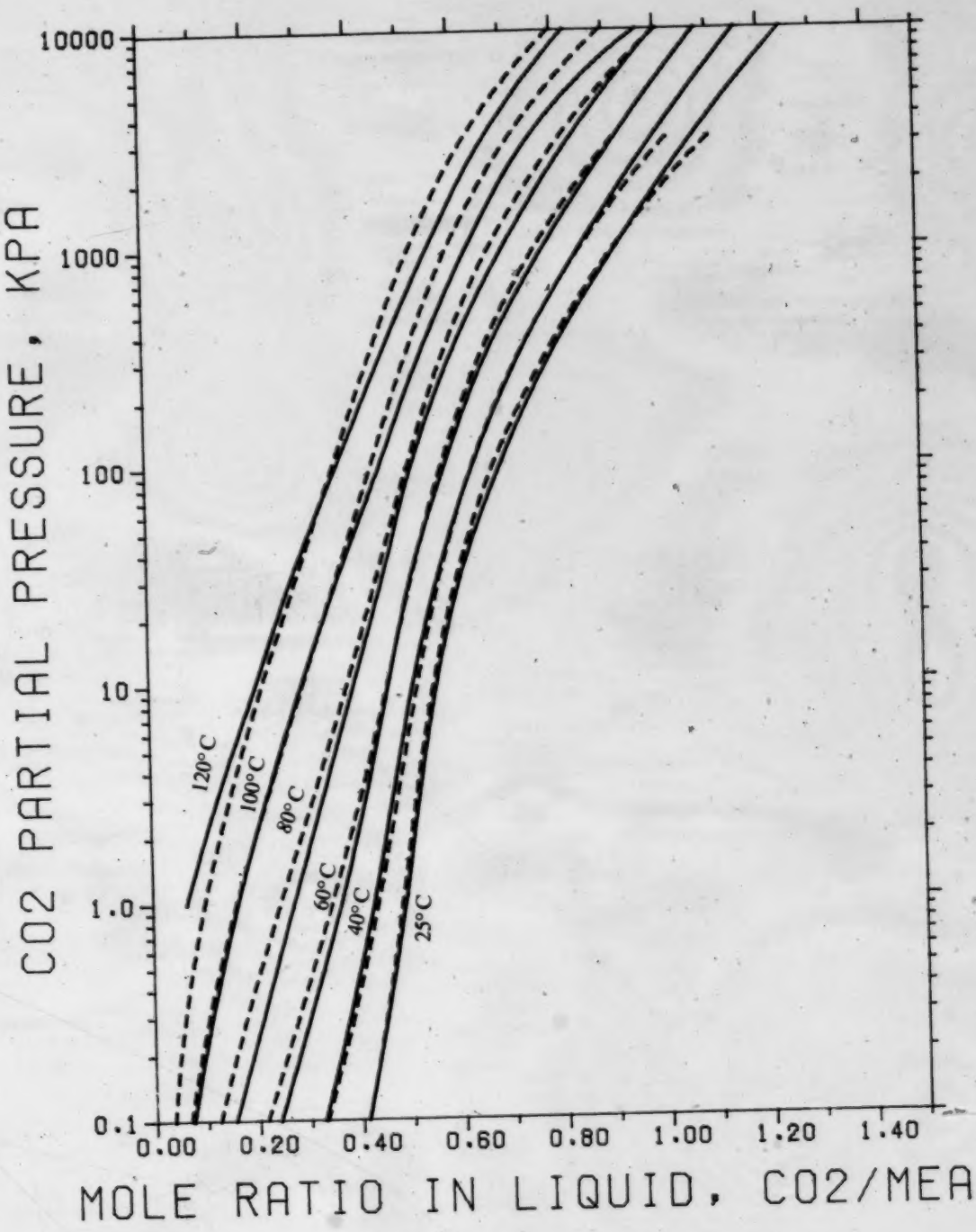

Figure 6.

SOLUBILITY OF CO2 IN 3.75 N MEA SOLUTIONS

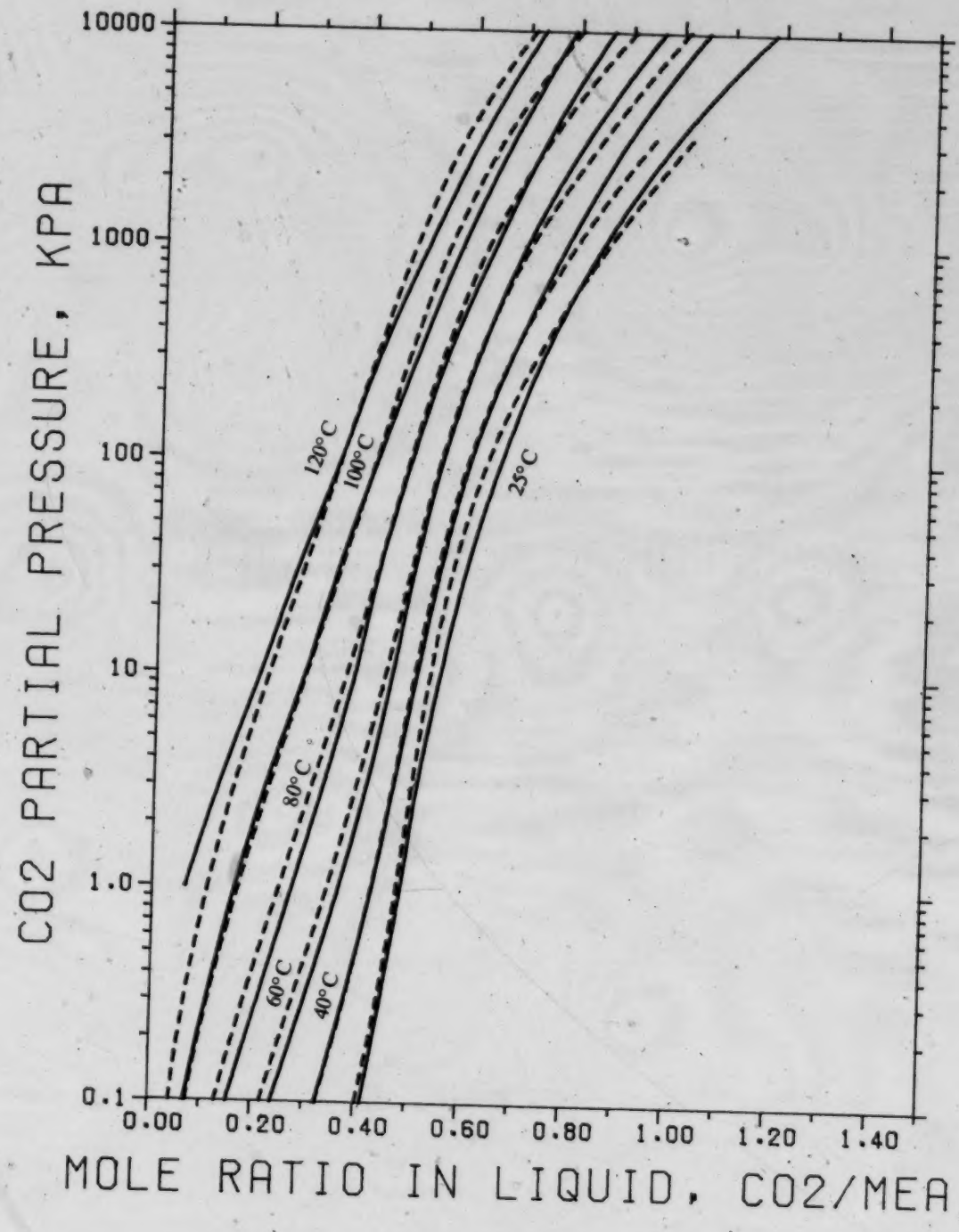

Figure 7.

SOLUBILITY OF CO2 IN 5.0 N MEA SOLUTIONS

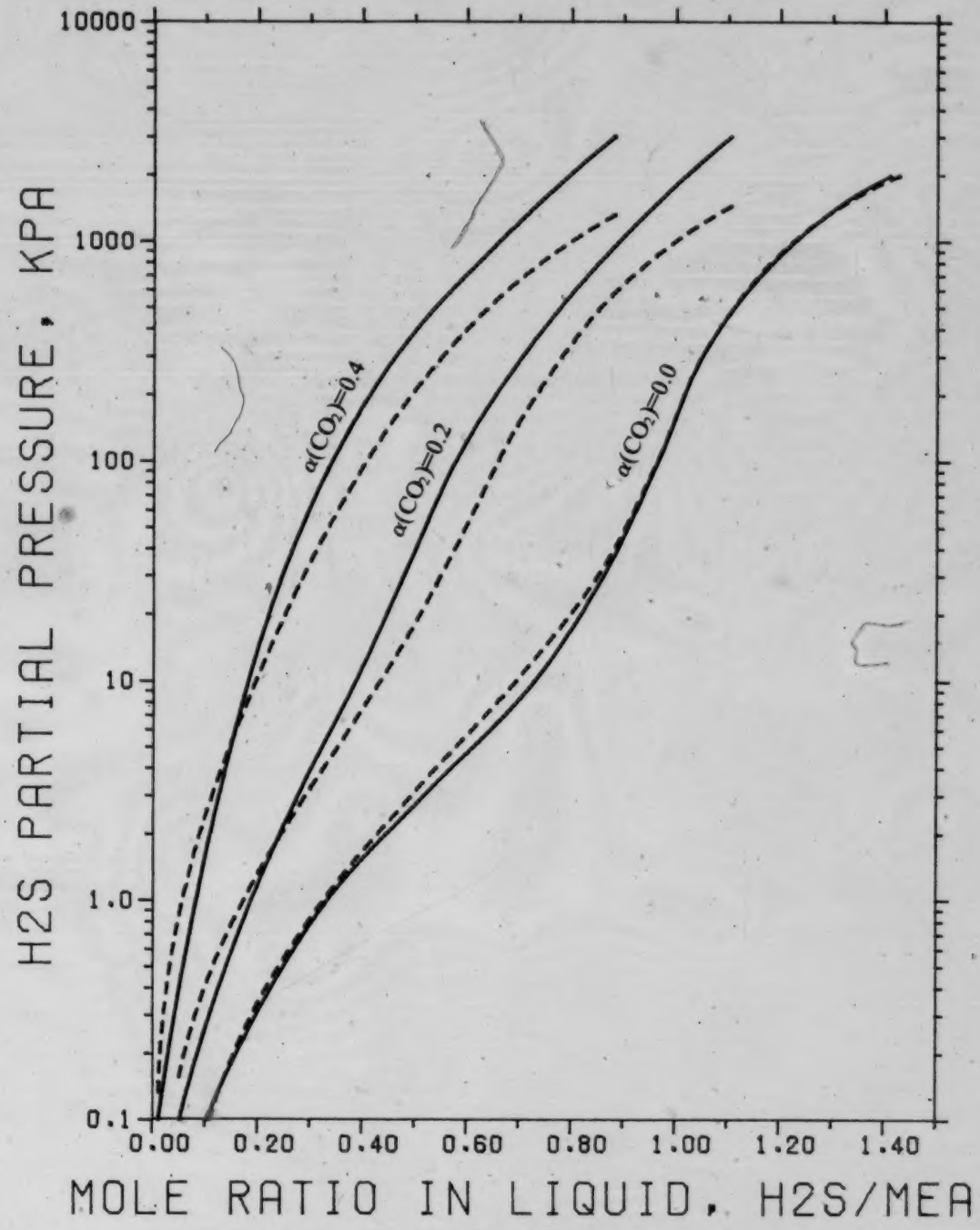

Figure 8.

EFFECT OF CO2 ON THE SOLUBILITY OF H2S
IN 2.5 N MEA SOLUTIONS AT 40 CELSIUS

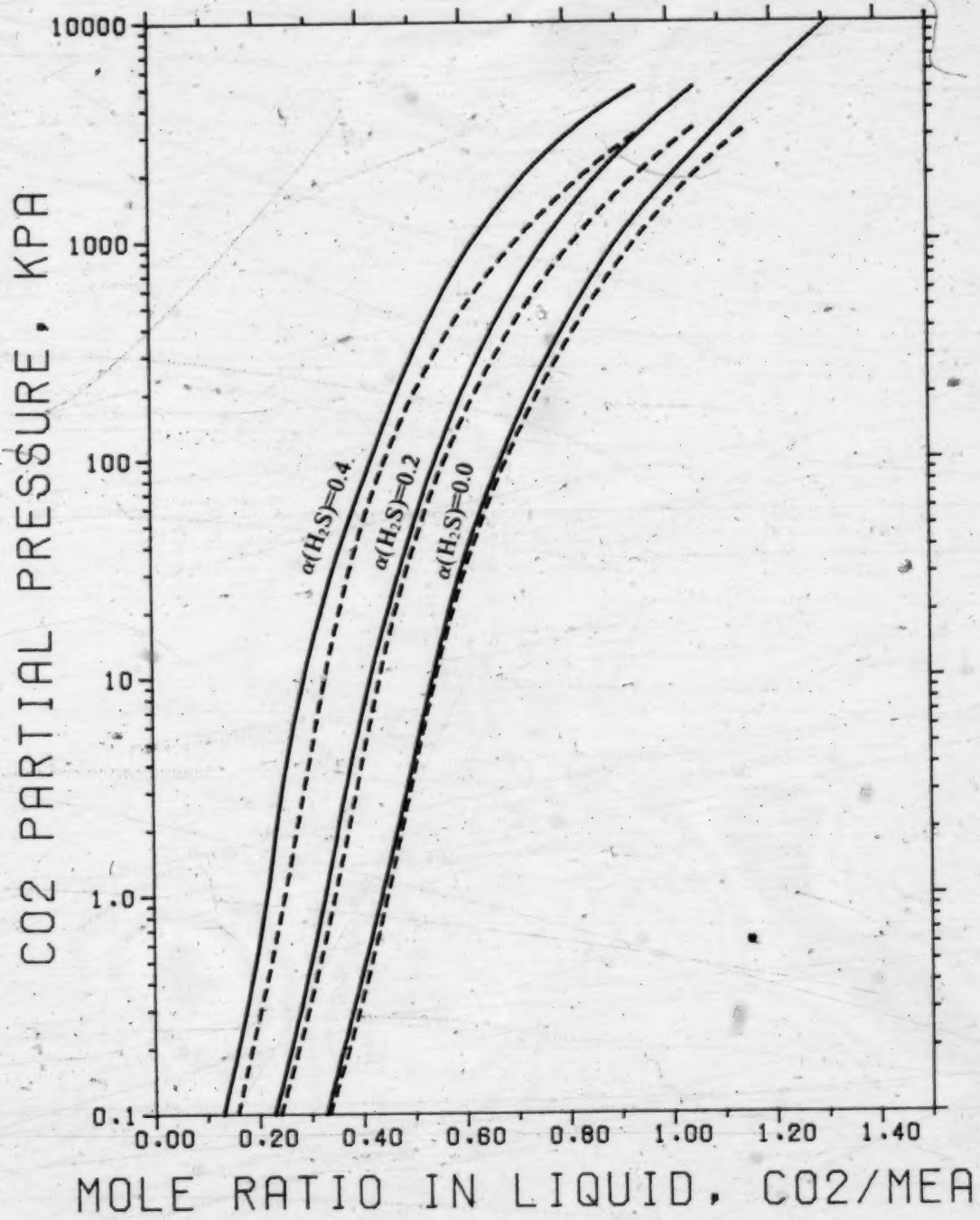

Figure 9.

EFFECT OF H2S ON THE SOLUBILITY OF CO2 IN 2.5 N MEA SOLUTIONS AT 40 CELSIUS

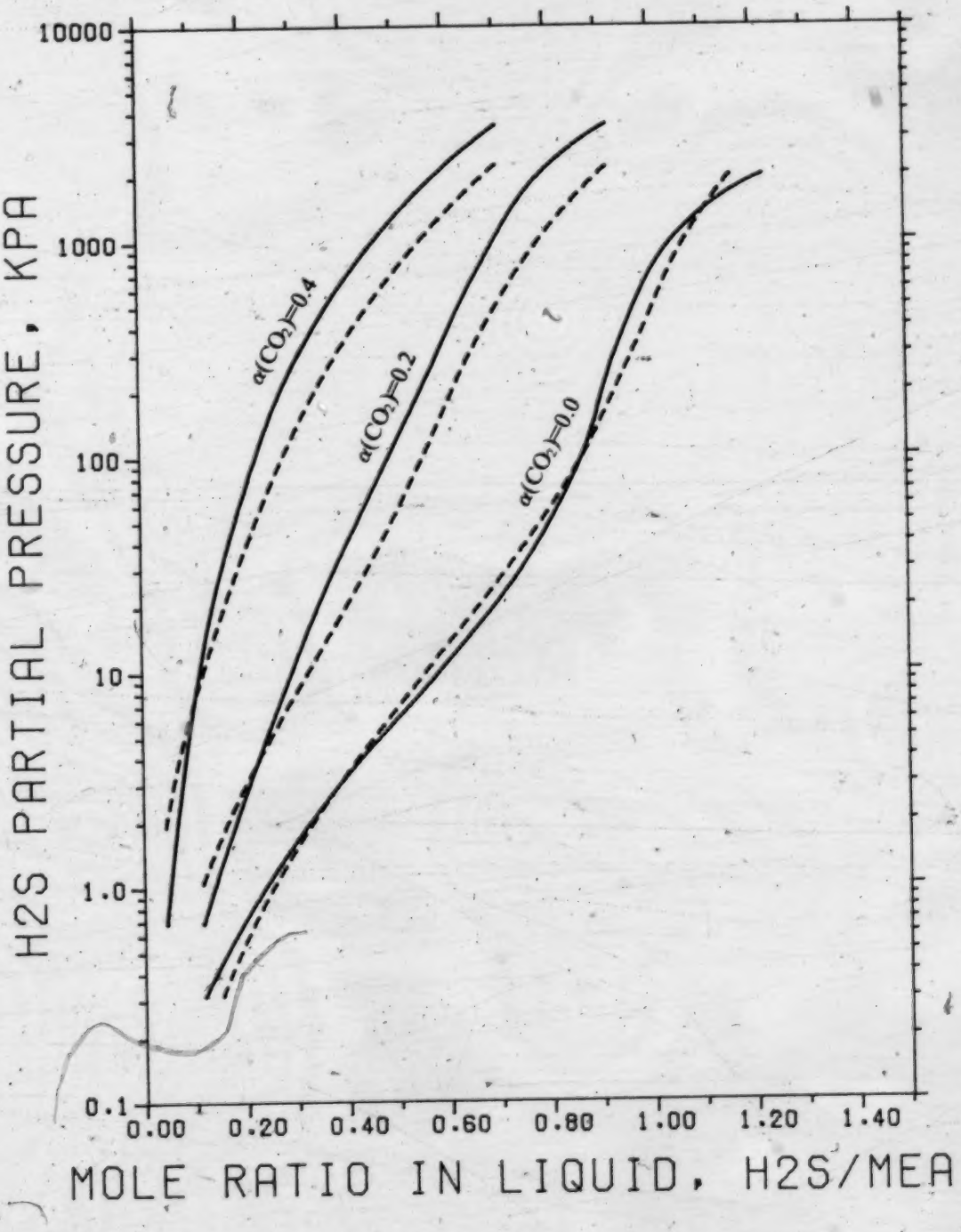

Figure 10.

EFFECT OF CO2 ON THE SOLUBILITY OF H2S
IN 5.0 N MEA SOLUTIONS AT 40 CELSIUS

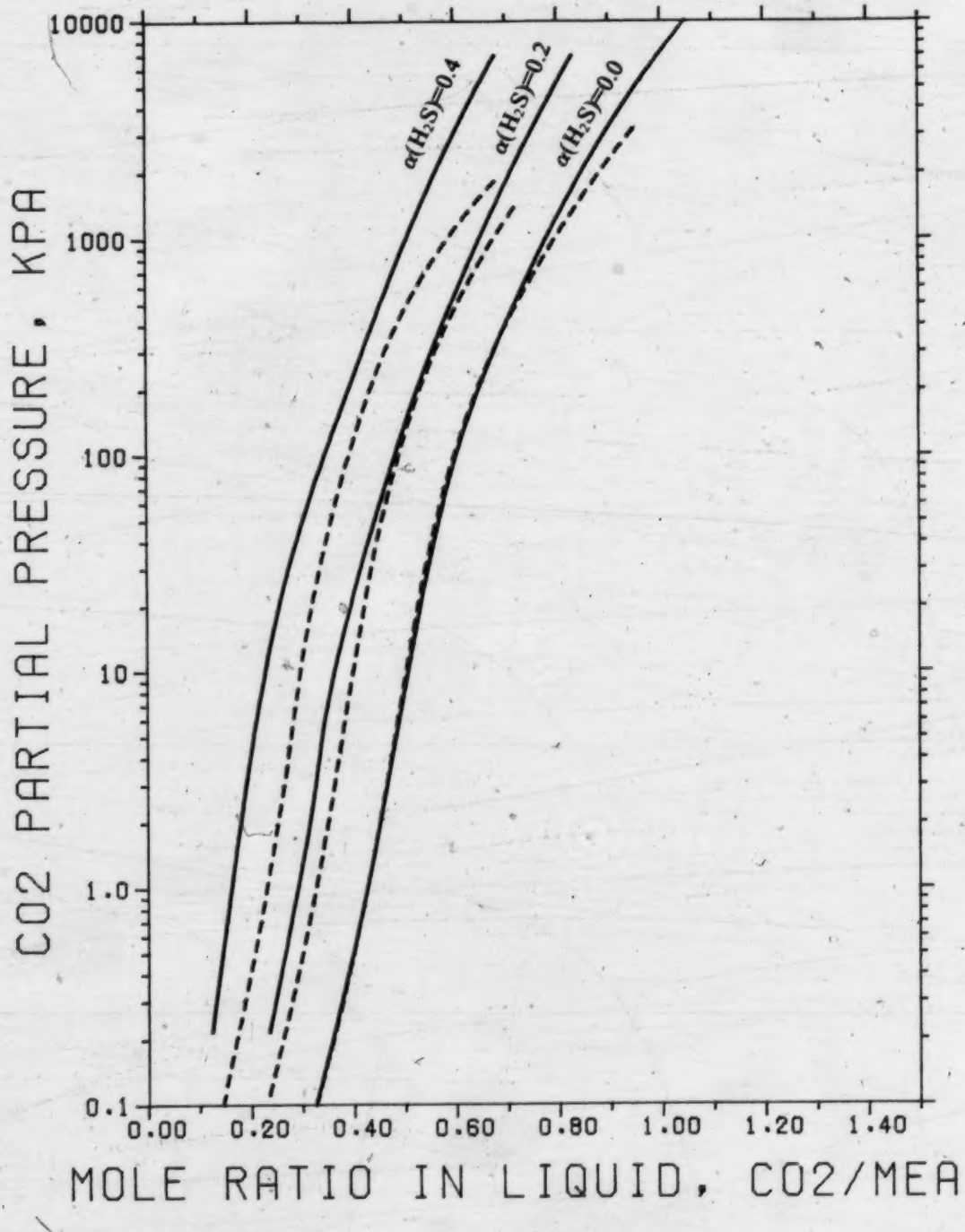

Figure 11.

EFFECT OF H2S ON THE SOLUBILITY OF CO2
IN 5.0 N MEA SOLUTIONS AT 40 CELSIUS .

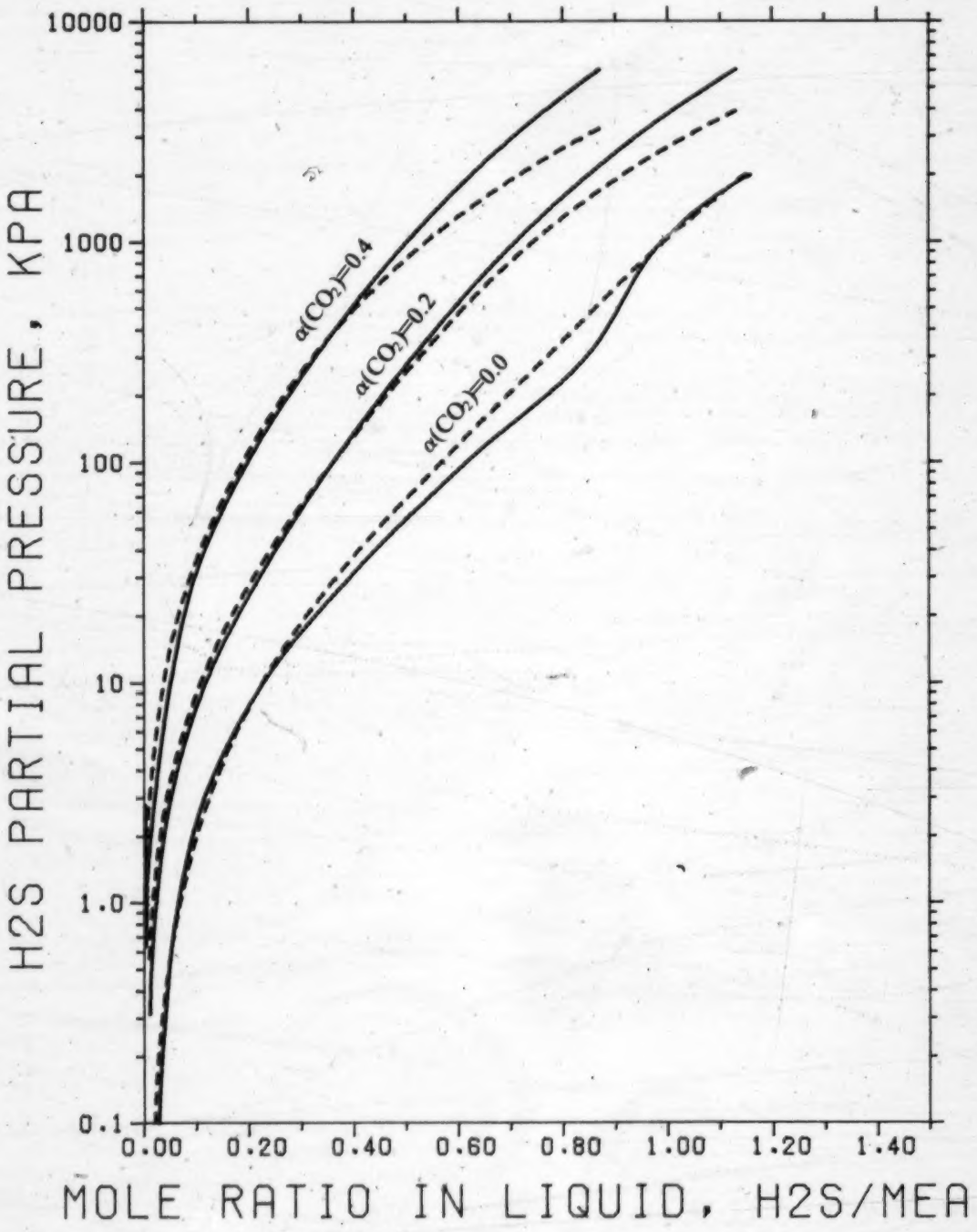

Figure 12.

EFFECT OF CO2 ON THE SOLUBILITY OF H2S IN 2.5 N MEA SOLUTIONS AT 100 CELSIUS

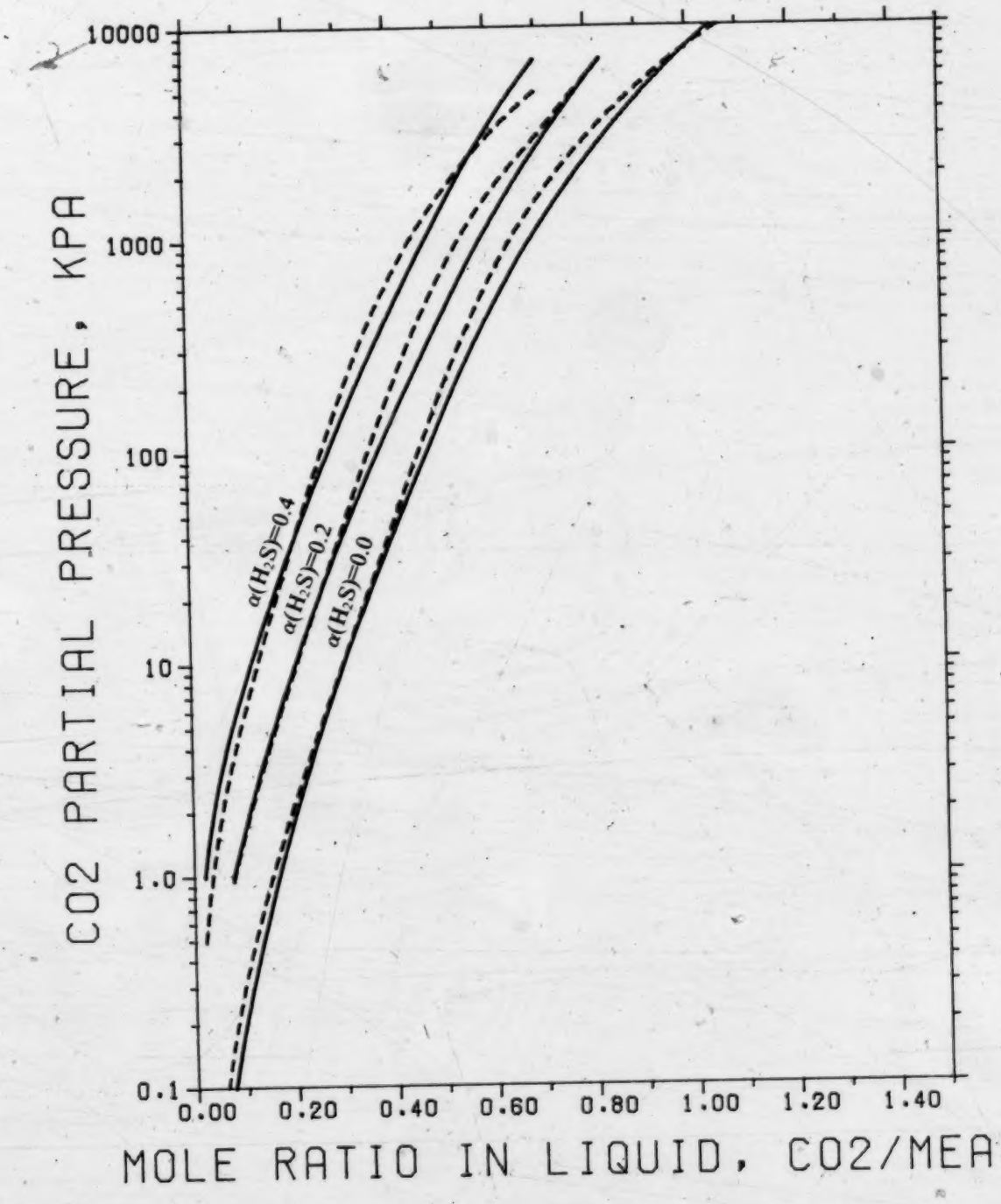

Figure 13.

EFFECT OF H2S ON THE SOLUBILITY OF CO2
IN 2.5 N MEA SOLUTIONS AT 100 CELSIUS

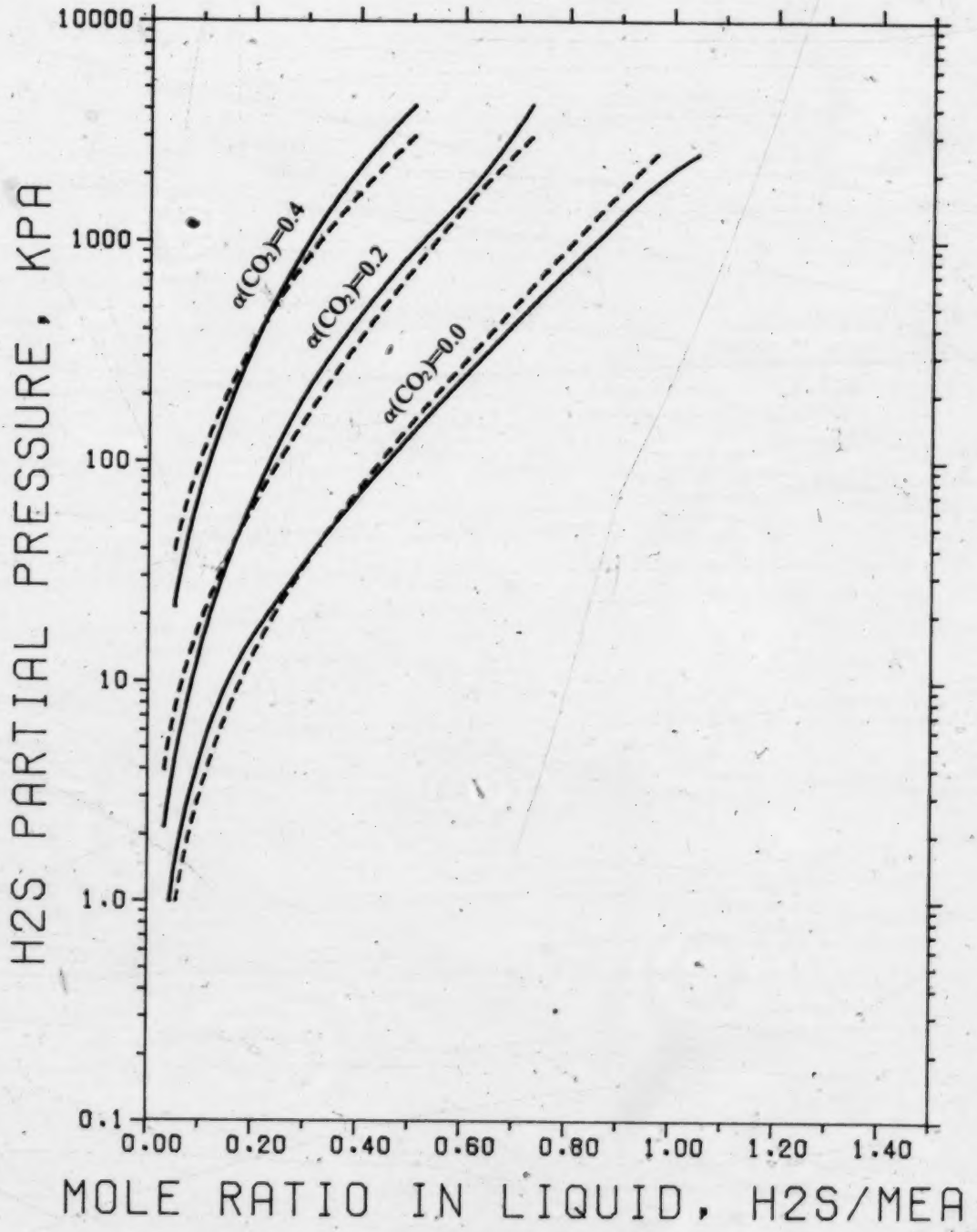

Figure 14.

EFFECT OF CO2 ON THE SOLUBILITY OF H2S
IN 5.0 N MEA SOLUTIONS AT 100 CELSIUS

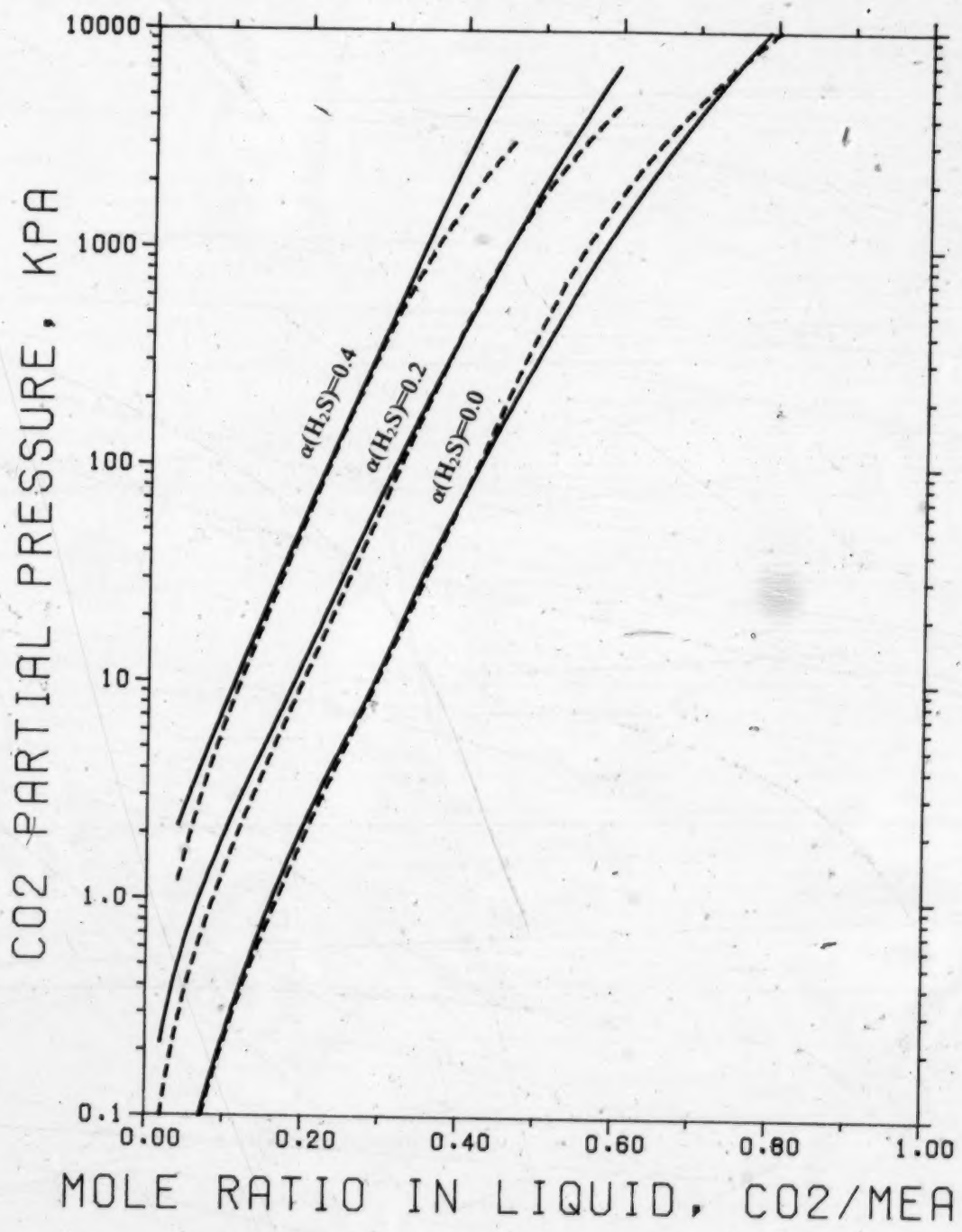

Figure 15.

EFFECT OF H2S ON THE SOLUBILITY OF CO2
IN 5.0 N MEA SOLUTIONS AT 100 CELSIUS

formation at 100°C, as well as the interaction parameters for the CO_2 / amine / water system were determined from their data. Figures 4, 5, 6 and 7 compare the predictions to the experimental data. The agreement is good at all normalities and temperatures.

The constants obtained from the single solute data were used to predict the equilibria for mixtures of carbon dioxide and hydrogen sulfide. Comparisons with the experimental data of Lee *et al.*, 1976c (2.5 *N* MEA solutions) and Lee *et al.*, 1975 (5.0 *N* MEA solutions) are shown in Figures 8 to 14. The agreement with experiment is much better at 100°C than at 40°C, probably because the carbamate formation is unimportant at the higher temperature. At 40°C, the agreement gets worse as the loading of the other acid gas increases. This is only to be expected because no mixture data have been used to determine the constants. It also suggests that the interaction parameters such as $\beta(CO_2\text{-}HS^-)$ and $\beta(H_2S\text{-}HCO_3^-)$ become important at high loadings. On the whole, the agreement is much better than that of the previous models. Generally, the predictions tend to bracket the experimental data. At loadings exceeding unity, however, the predicted partial pressures are usually lower than the the experimental values.

The most likely direction for improving the predictions seems to be the inclusion of parameters involving CO_2 and H_2S. This would require the equilibrium data for the CO_2 / H_2S / water system. Unfortunately, there are very few data available for this system. It would be very helpful to have reliable experimental data for the carbamate formation.

2. Solubility of acid gases in DIPA solutions

Isaacs *et al.* (1977a and 1977b) have reported the solubility of carbon dioxide, hydrogen sulfide and their mixtures in 2.5 *N* DIPA solutions at 40 and 100°C. Their data for the pure components as well as mixtures were used to deduce the binary interaction parameters and the equilibrium constants. These are presented in Table 2.

The fitted equilibrium constants for DIPA are of the same order magnitude as the measured equilibrium constants for MEA and DEA. Figures 16, 17, 18 and 19 compare the predictions made by using these constants to experimental data. As compared to MEA, there is a noticeable improvement in accuracy, particularly for mixtures. The predictions at very low mole ratios in the liquid phase (less than 0.1) are not as good as those at moderate or high loadings. This fact can not be considered significant because much of the data for low loadings were obtained by extrapolation and not by direct measurement.

3. Solubility of acid gases in DEA solutions

Lee *et al.* have measured the solubility of mixtures of carbon dioxide and hydrogen sulfide in DEA solutions. Their data for the solubility of carbon dioxide and hydrogen sulfide were used to obtain the binary interaction parameters and the equilibrium constants. These constants are presented in Table 2. Figures 20 to 27 show the predictions and the experimental solubility data for 2.0 and 3.5 *N* DEA solutions at 50 and 100°C.

The predictions of the solubility of the carbon dioxide in 3.5 *N* DEA solutions are

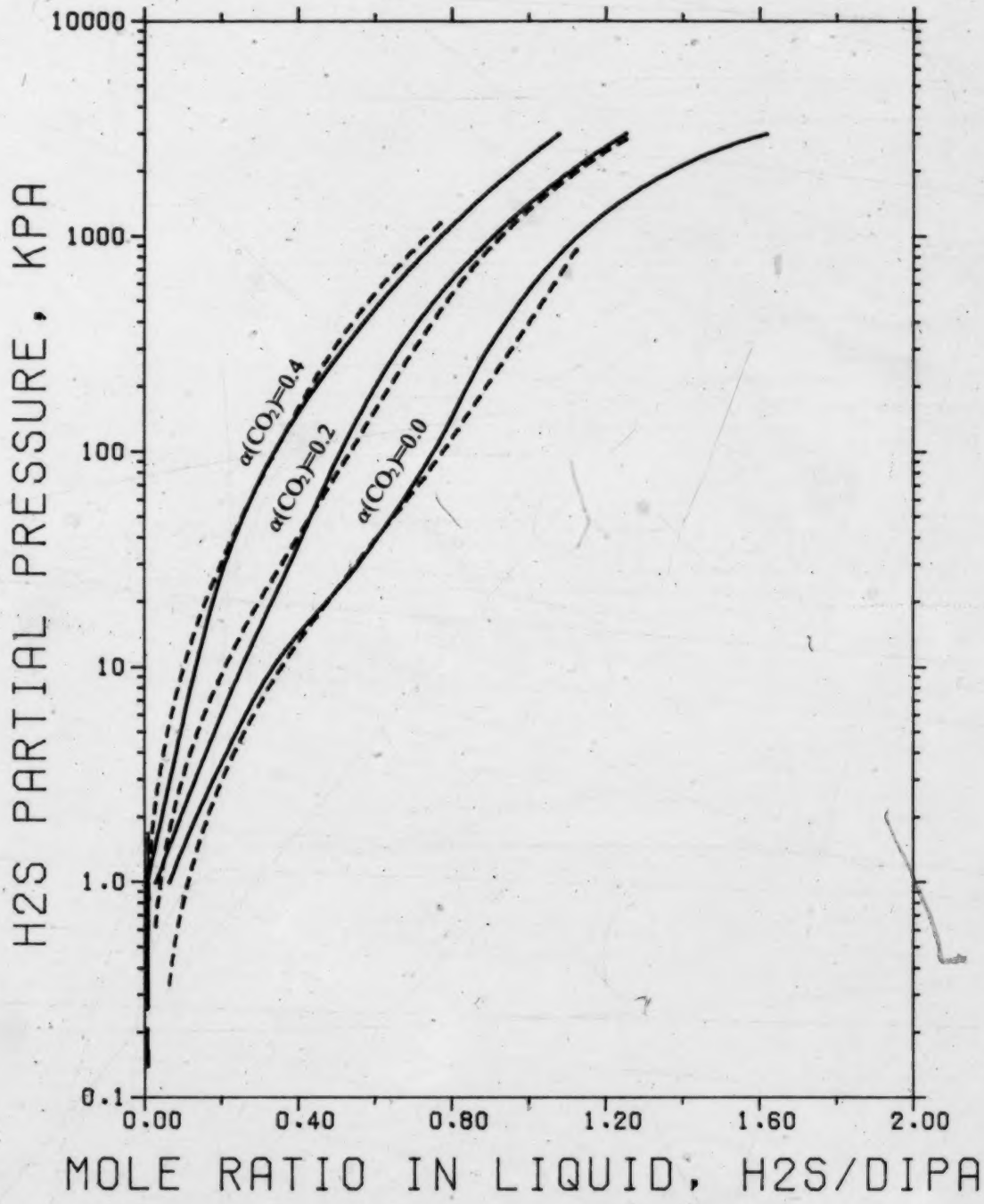

Figure 16.

EFFECT OF CO2 ON THE SOLUBILITY OF H2S
IN 2.5 N DIPA SOLUTIONS AT 40 CELSIUS

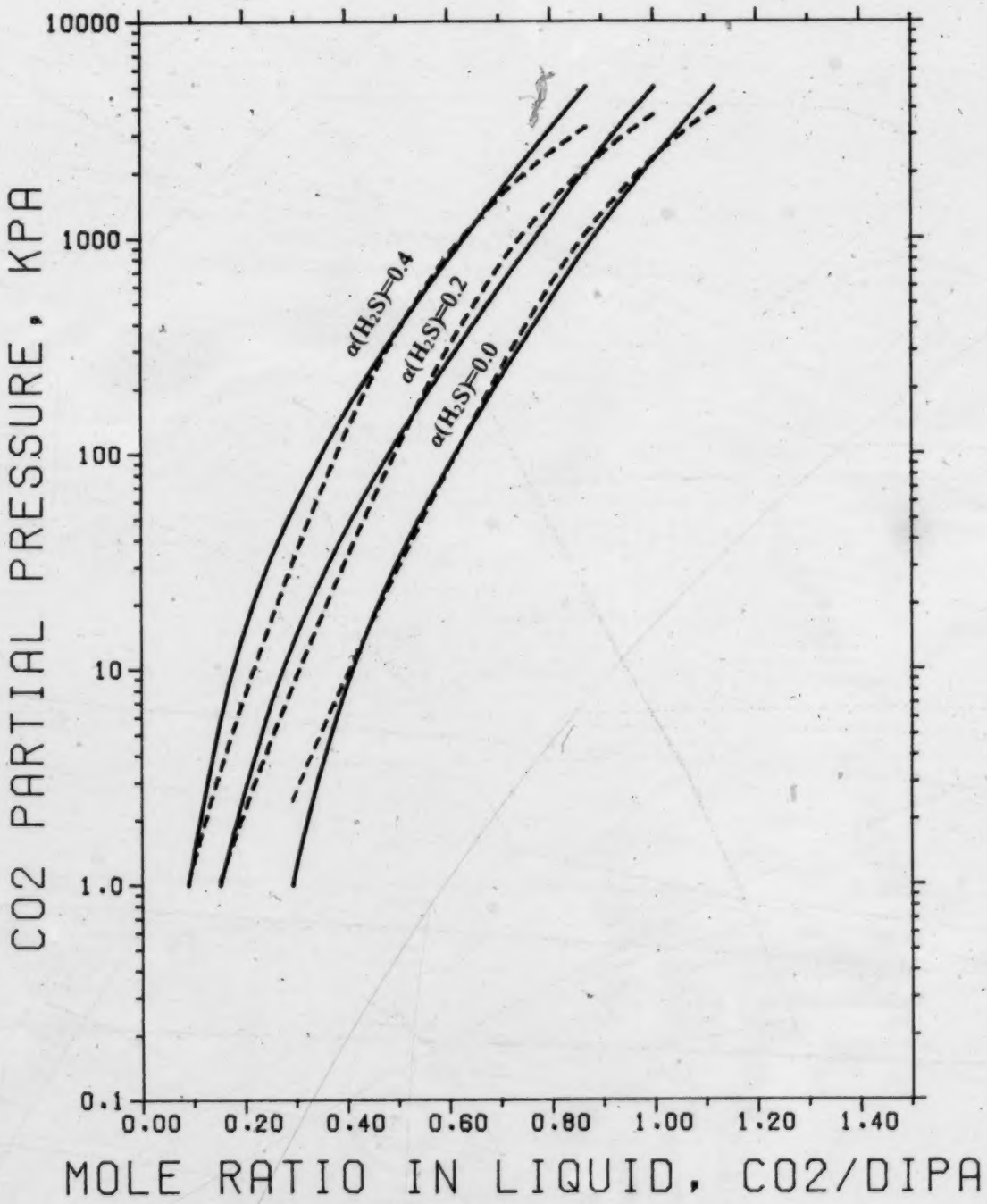

Figure 17.

EFFECT OF H2S ON THE SOLUBILITY OF CO2
IN 2.5 N DIPA SOLUTIONS AT 40 CELSIUS

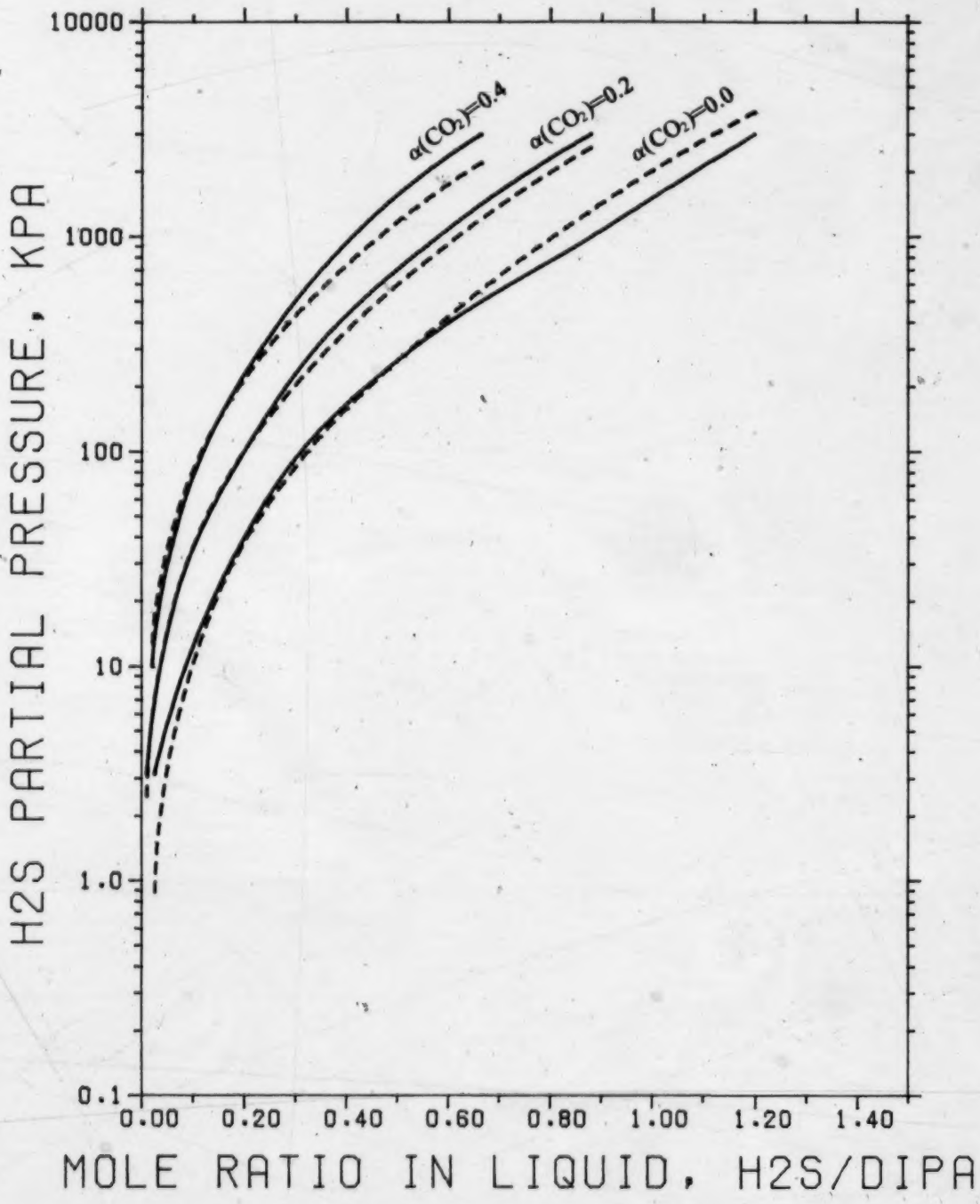

Figure 18.

EFFECT OF CO2 ON THE SOLUBILITY OF H2S
IN 2.5 N DIPA SOLUTIONS AT 100 CELSIUS

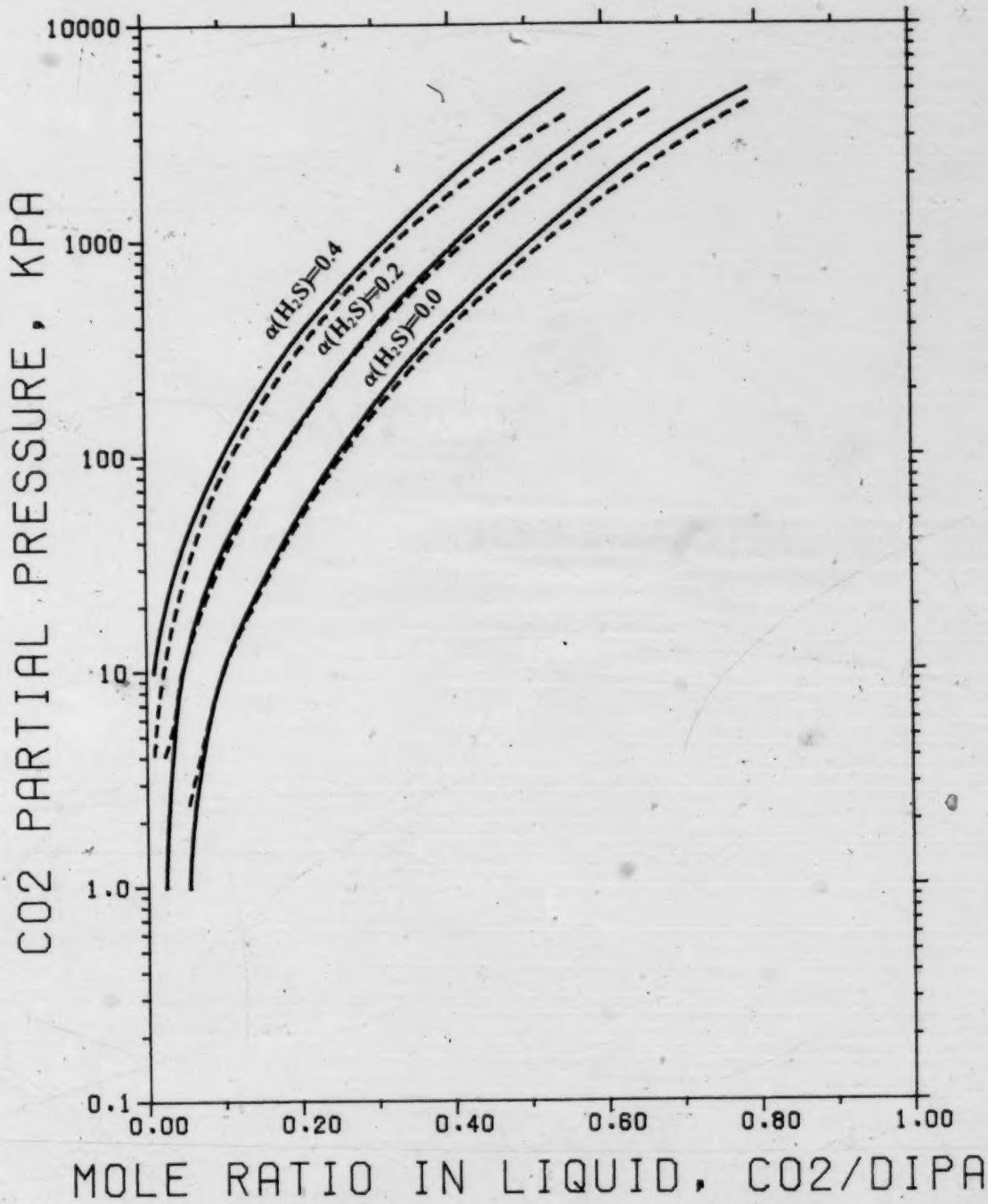

Figure 19.

EFFECT OF H2S ON THE SOLUBILITY OF CO2
IN 2.5 N DIPA SOLUTIONS AT 100 CELSIUS

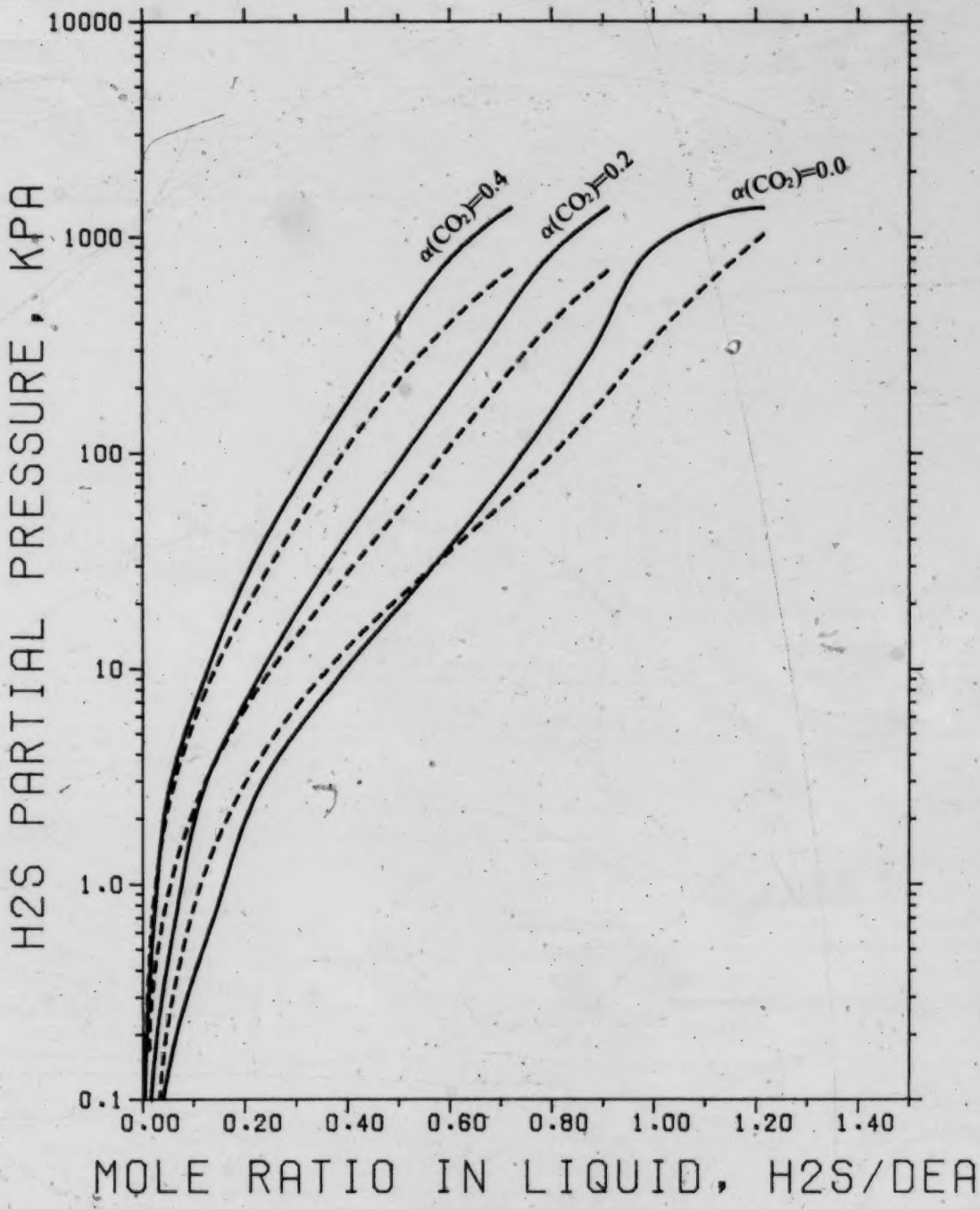

Figure 20.

EFFECT OF CO2 ON THE SOLUBILITY OF H2S
IN 2.0 N DEA SOLUTIONS AT 50 CELSIUS

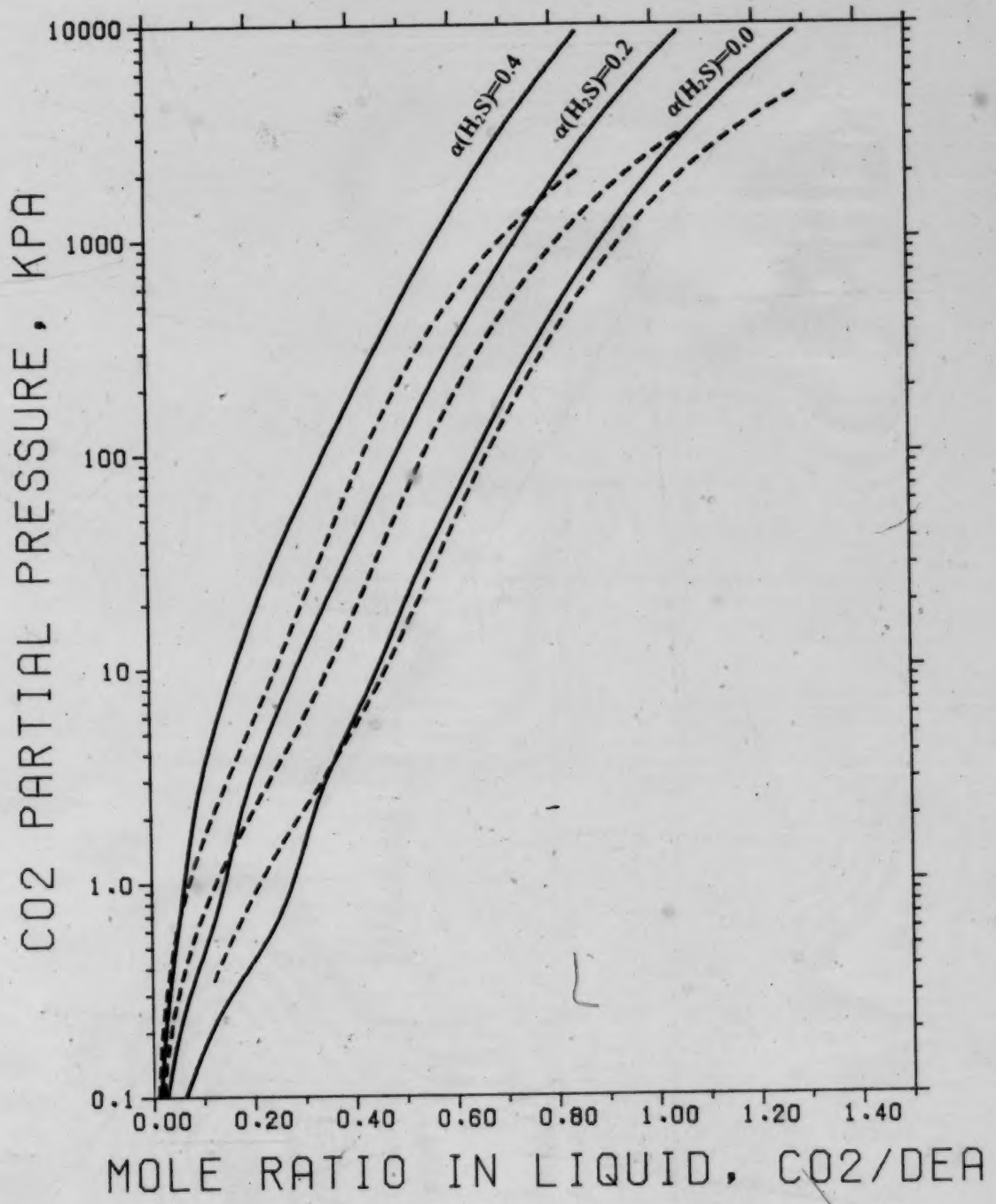

Figure 21.

EFFECT OF H2S ON THE SOLUBILITY OF CO2
IN 2.0 N DEA SOLUTIONS AT 50 CELSIUS

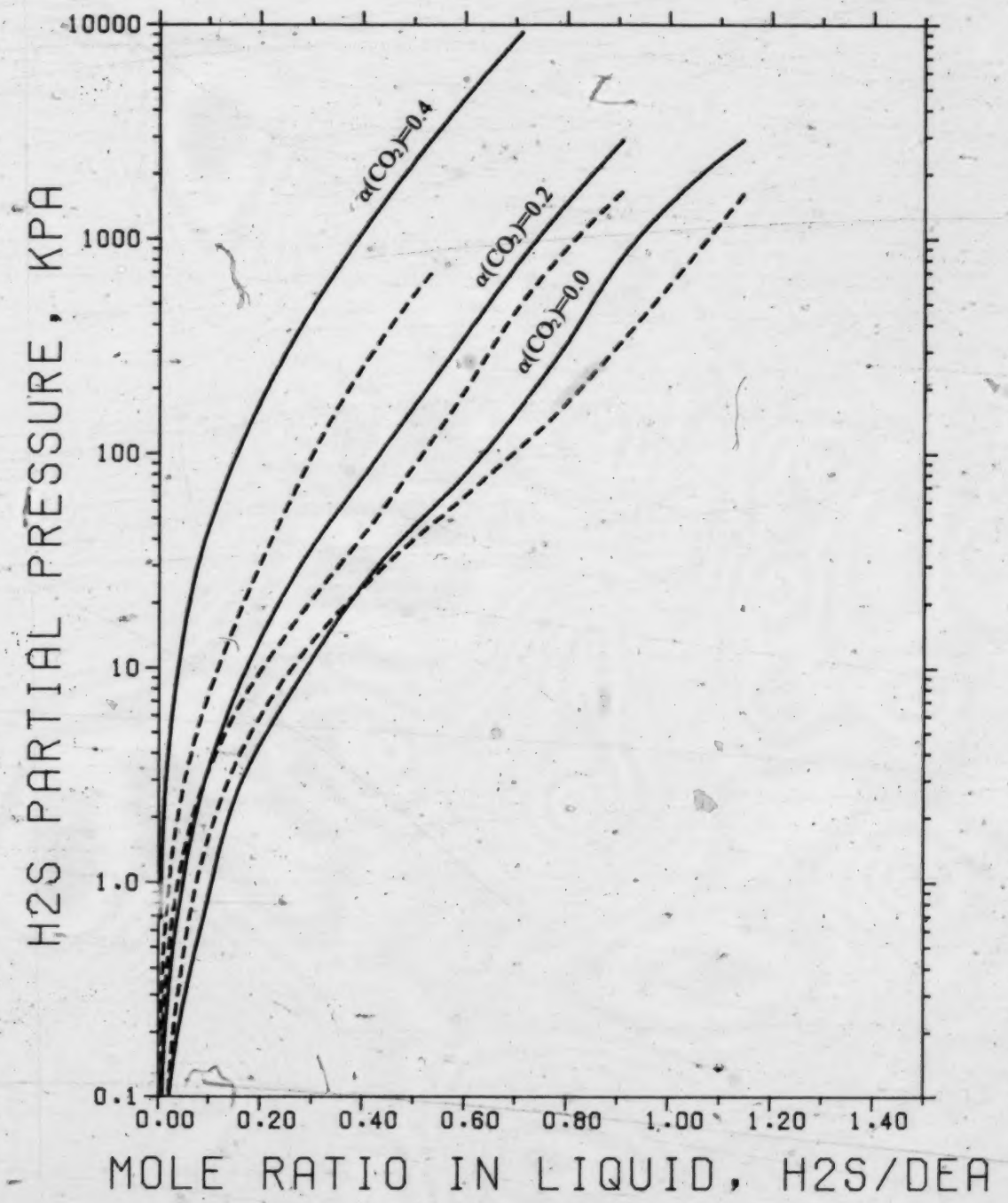

Figure 22.

EFFECT OF CO2 ON THE SOLUBILITY OF H2S
IN 3.5 N DEA SOLUTIONS AT 50 CELSIUS

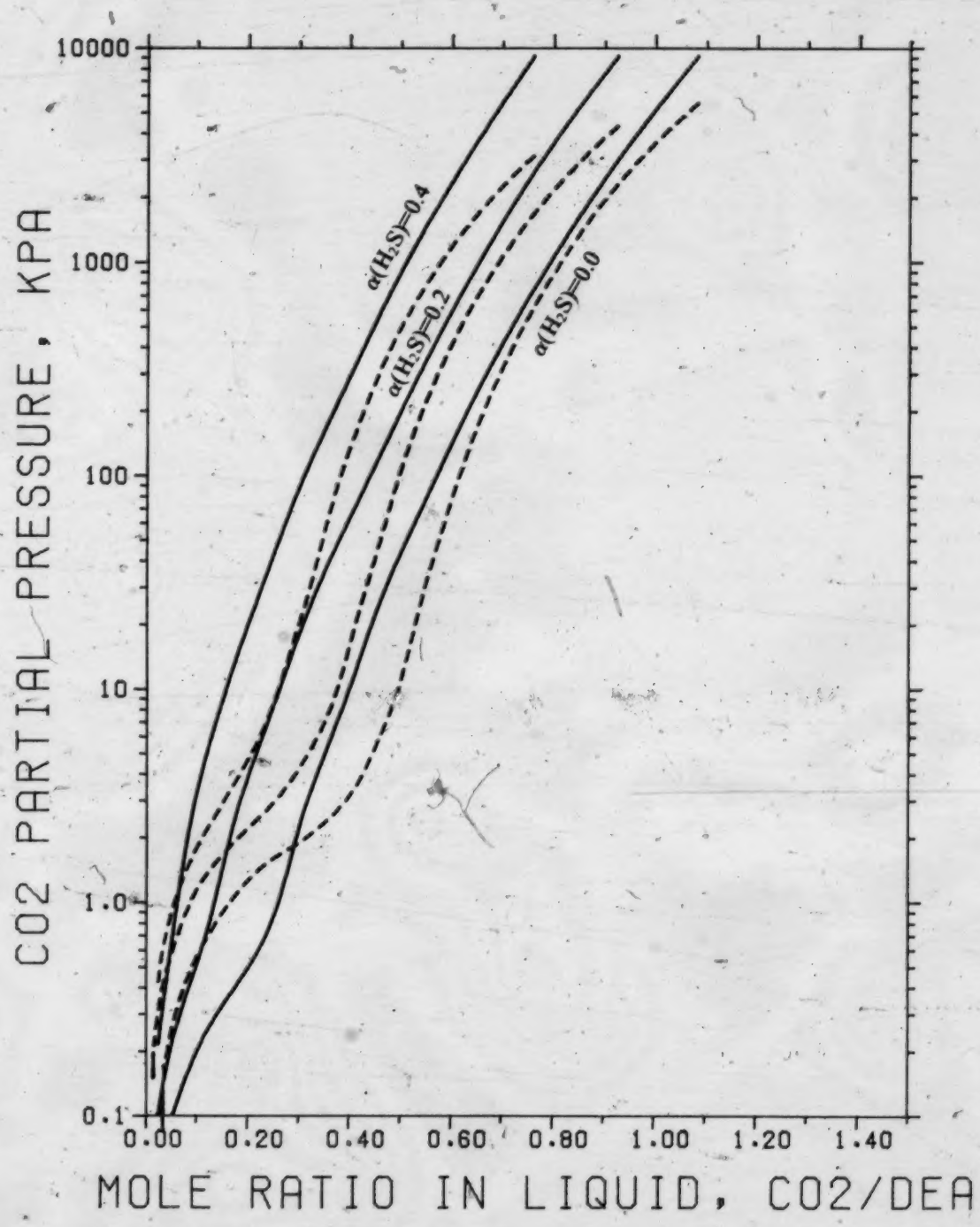

Figure 23.

EFFECT OF H2S ON THE SOLUBILITY OF CO2
IN 3.5 N/DEA SOLUTIONS AT 50 CELSIUS

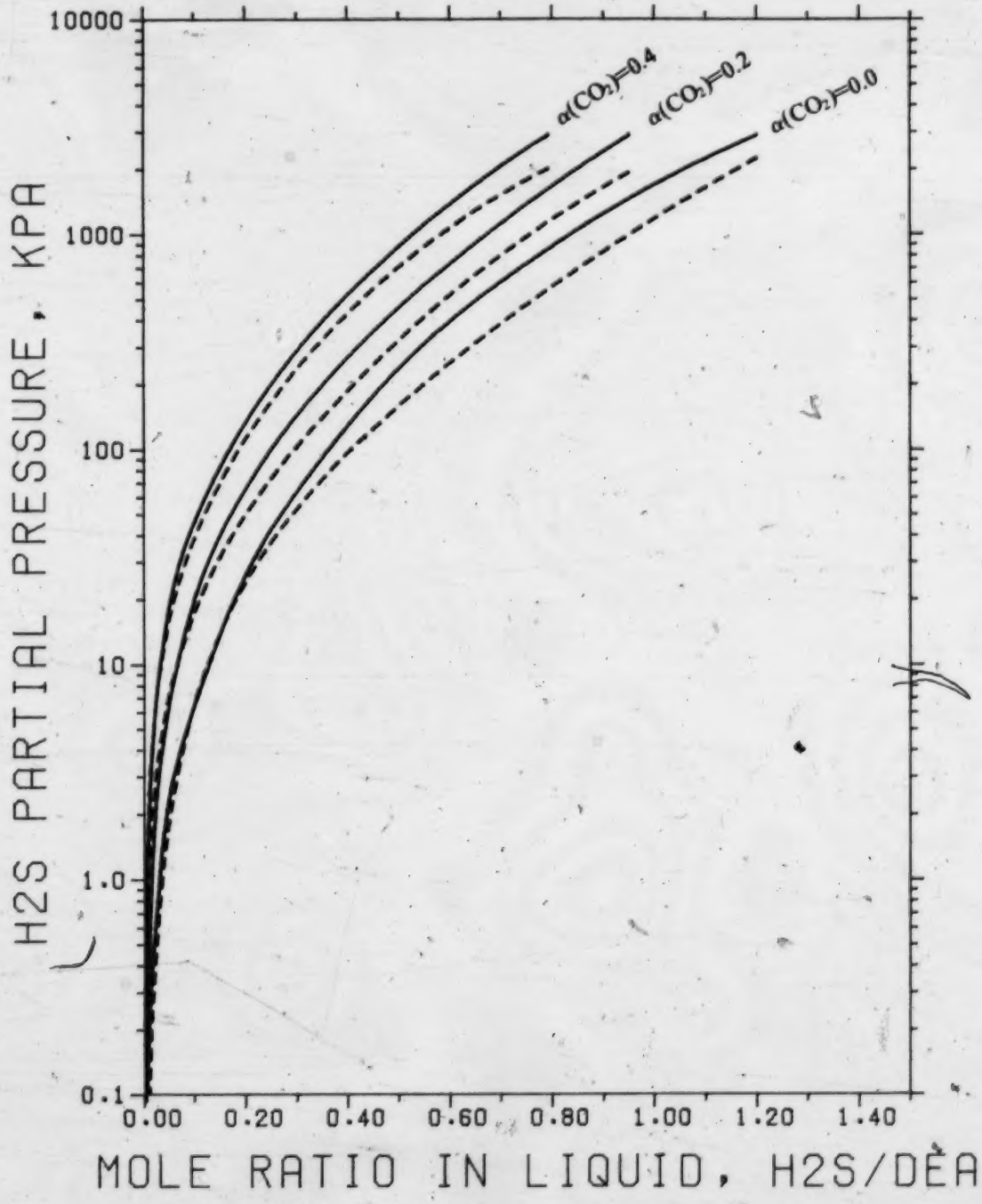

Figure 24.

EFFECT OF CO2 ON THE SOLUBILITY OF H2S
IN 2.0 N DEA SOLUTIONS AT 100 CELSIUS

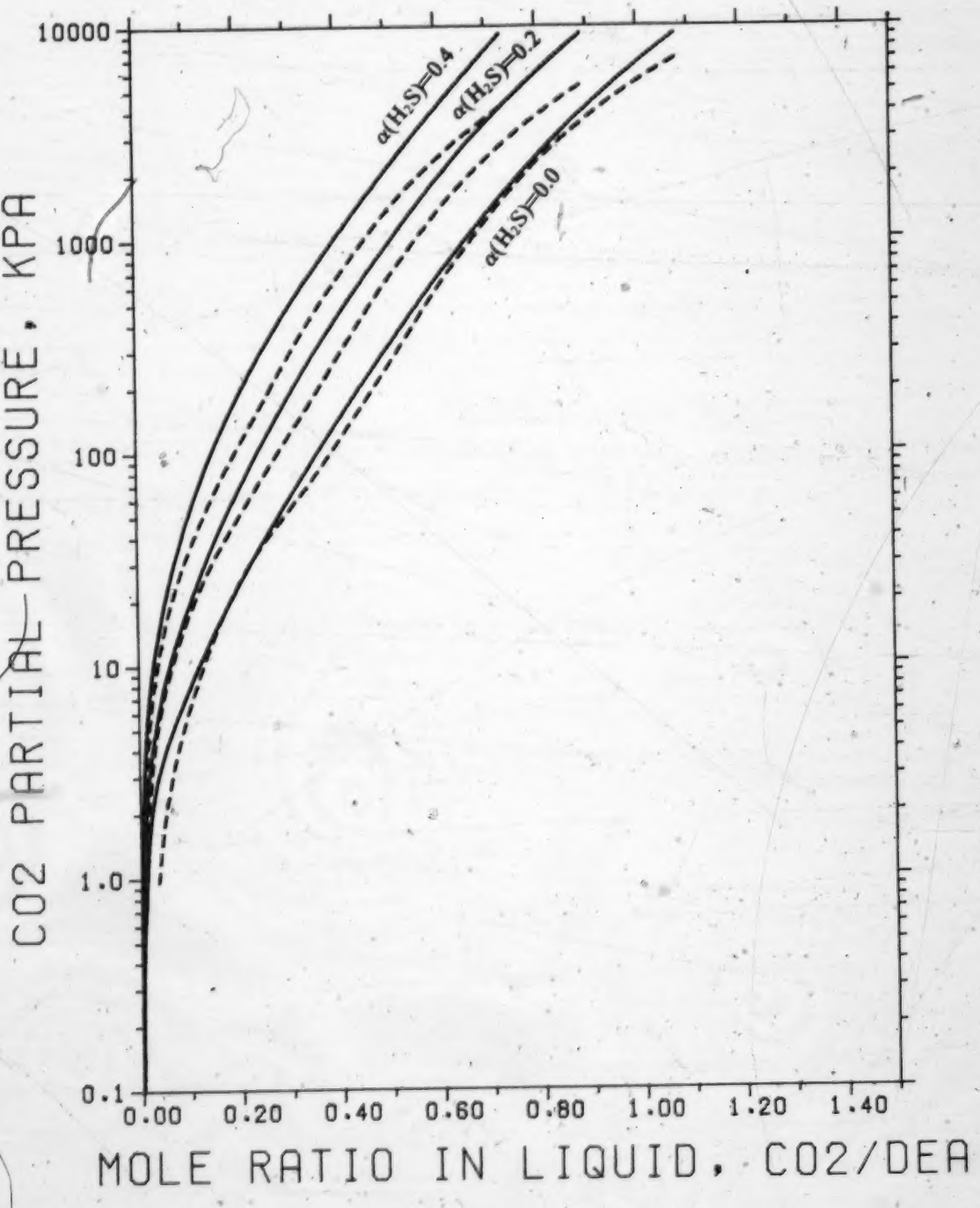

Figure 25.

EFFECT OF H2S ON THE SOLUBILITY OF CO2 IN 2.0 N DEA SOLUTIONS AT 100 CELSIUS

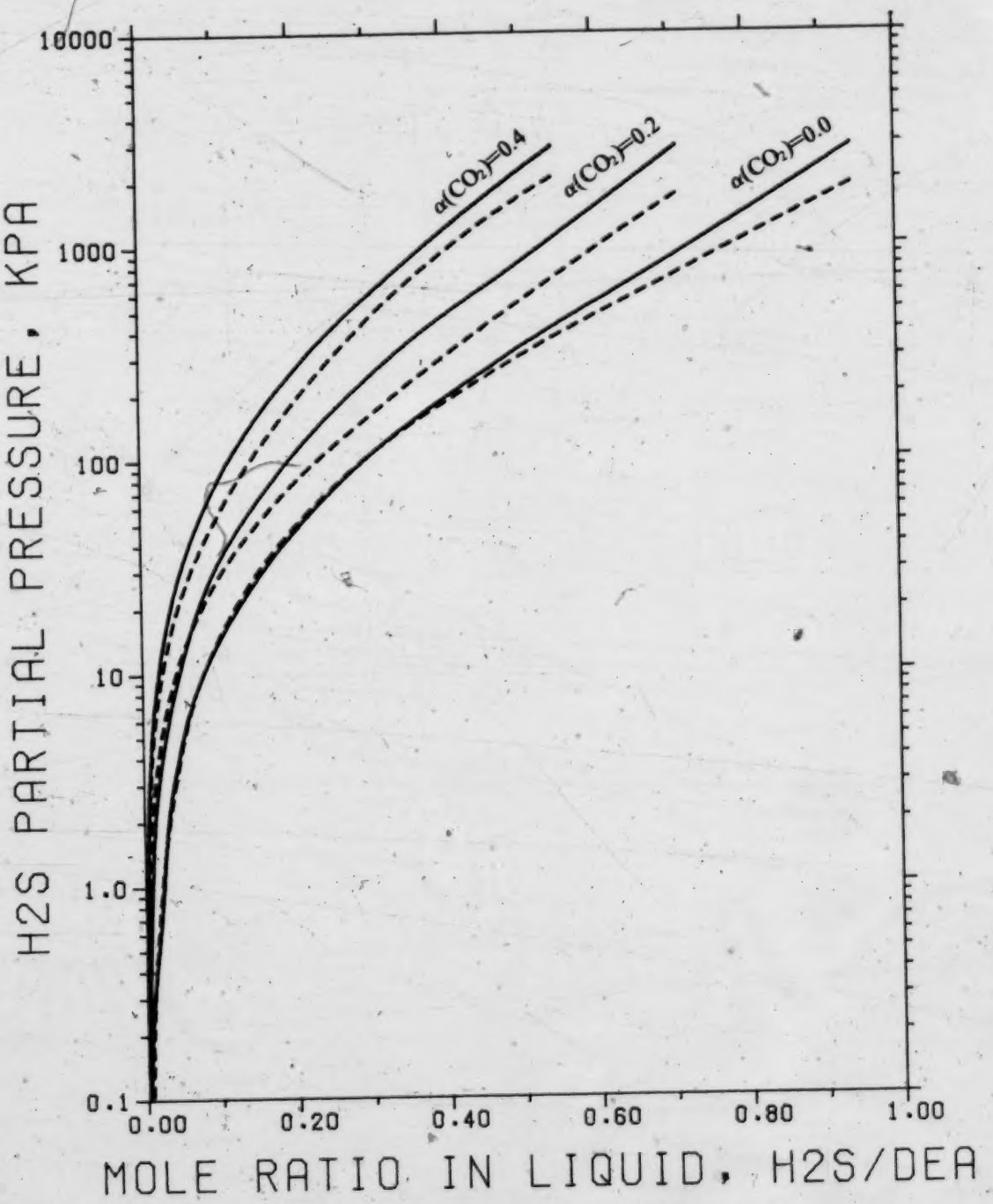

Figure 26.

EFFECT OF CO2 ON THE SOLUBILITY OF H2S
IN 3.5 N DEA SOLUTIONS AT 100 CELSIUS

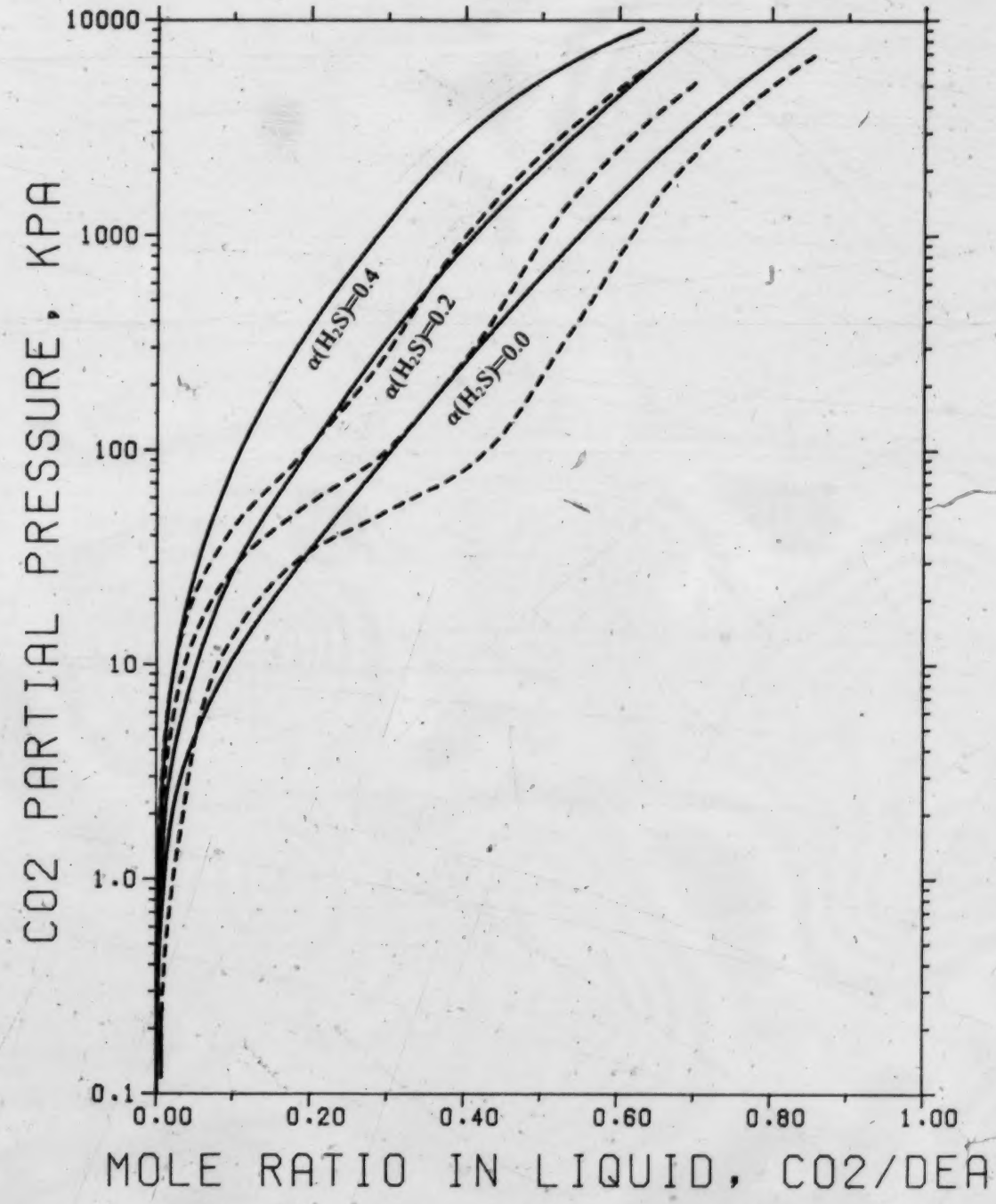

Figure 27.

EFFECT OF H2S ON THE SOLUBILITY OF CO2
IN 3.5 N DEA SOLUTIONS AT 100 CELSIUS

poor. Other predictions are in close agreement with the experimental data. As with MEA, the agreement gets poorer as the mole ratio of the other acid gas increases. It is likely that the agreement will be improved if the mixture data is used to determine the interaction parameters.

Table 2. Specific interaction parameters

Monoethanolamine

$\beta(RR'NH\text{-}HS^-)$=-0.0375,
$\beta(RR'NH_2^+\text{-}HS^-)$=0.005,
$\beta(RR'NH\text{-}HCO_3^-)$=-0.0245,
$\beta(RR'NH_2^+\text{-}HCO_3^-)$=-0.0375,
$\beta(RR'NH\text{-}RR'NCOO^-)$=-0.063,
$\beta(RR'NH_2^+\text{-}RR'NCOO^-)$=0.006,

Diethanolamine

$\beta(RR'NH\text{-}HS^-)$=0.029845,
$\beta(RR'NH_2^+\text{-}HS^-)$=0.00482,
$\beta(RR'NH\text{-}HCO_3^-)$=0.00534,
$\beta(RR'NH_2^+\text{-}HCO_3^-)$=-0.041,
$\beta(RR'NH\text{-}RR'NCOO^-)$=0.2601,
$\beta(RR'NH_2^+\text{-}RR'NCOO^-)$=-0.04288,

Diisopropanolamine

$\beta(RR'NH\text{-}HS^-)$=0.0921,
$\beta(RR'NH_2^+\text{-}HS^-)$=0.0905,
$\beta(RR'NH\text{-}HCO_3^-)$=0.309,
$\beta(RR'NH_2^+\text{-}HCO_3^-)$=0.103,
$\beta(RR'NH\text{-}RR'NCOO^-)$=-0.00294,
$\beta(RR'NH_2^+\text{-}RR'NCOO^-)$=0.1098,

VI. CONCLUSIONS

The solubility model presented here is consistent with the thermodynamic criteria for the equilibrium in multicomponent, multiphase systems. The binary interaction parameters required in the model are easily determined from the experimental data. The equilibrium constants can also be determined from the solubility data. The equilibrium data for the pure components or for the mixtures may be used to determine the interaction parameters. The computer program developed in this work is efficient and general. It can be used to compute the equilibrium composition in any multicomponent system if the equilibrium constants, Henry's constants and the interaction parameters are known.

The predictions made using this model are better than those of the Kent and Eisenberg and the Klyamer *et al.* models. The agreement for the mixtures is improved if the mixture data are used to calculate the interaction parameters.

The model uses the dielectric constant of pure water in the Debye-Huckel expression where the dielectric constant of the solution is required. For this assumption to be valid, the concentrations of the solute species must remain low. The activity coefficient of water has been assumed to be unity. This requires the mole fraction of water in the liquid phase to be close to unity. The validity of the model also depends upon the assumed reaction mechanism. For example, if the pH is more than 11, the hydroxyl group of the alkanolamines also reacts with the acid gases.

Many of the equilibrium constants required in the model have been measured only in a narrow range of temperatures. Experimental measurements of these constants upto 120°C are certainly desirable. Solubility data for the CO_2 / H_2S / water system and for the CO_2 / H_2S / amine / water system are also needed to verify the validity of the model for these systems. More binary interaction parameters should be included in the model to improve the predictions for the high loadings.

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APPENDIX A

Klyamer *et al.* Model

The Klyamer *et al.* model is based on the assumption that the activity coefficients of all ions in the liquid phase are equal. The expressions for the partial pressures are derived below.

Reactions:

$RR'NH + H_2O = RR'NH_2^+ + OH^-$

$H_2S = H^+ + HS^-$

$H_2O = H^+ + OH^-$

$HS^- = H^+ + S^=$

$2\ RR'NH + CO_2 = RR'NH_2^+ + RR'NCOO^-$

$H_2O + CO_2 = H^+ + HCO_3^-$

$HCO_3^- = H^+ + CO_3^=$

Conservation equations:

$$[RR'NH_2^+] + [H^+] = [HCO_3^-] + [RR'NCOO^-] + [OH^-] + [HS^-] + 2\,[CO_3^=] + 2\,[S^=] \quad \text{— (A.62)}$$

$$m_A = [RR'NH] + [RR'NH_2^+] + [RR'NCOO^-] \quad \text{— (A.63)}$$

$$m_A\, x(CO_2) = [CO_2] + [HCO_3^-] + [RR'NCOO^-] + [CO_3^=] \quad \text{— (A.64)}$$

$$m_A\, x(H_2S) = [H_2S] + [HS^-] + [S^=] \quad \text{— (A.65)}$$

$$K_i = \gamma^2\,[RR'NH_2^+]\,[OH^-] \,/\, a\,\alpha^2\,[RR'NH] \quad \text{— (A.66)}$$

$$K_W = \gamma^2\,[H^+]\,[OH^-] \,/\, \alpha \quad \text{— (A.67)}$$

$$K_{1C} = \gamma^2\,[H^+]\,[HS^-] \,/\, [H_2S] \quad \text{— (A.68)}$$

$$K_{2C} = \gamma\,[H^+]\,[S^=] \,/\, [HS^-] \quad \text{— (A.69)}$$

$$H'(H_2S) = [H_2S] \,/\, p(H_2S) \quad \text{— (A.70)}$$

$$K_M = \gamma^2\,[RR'NH_2^+]\,[RR'NCOO^-] \,/\, a^2\,\alpha^2\,[RR'NH]^2\,p(CO_2) \quad \text{— (A.71)}$$

$$K_{1Y} = \gamma^2\,[H^+]\,[HCO_3^-] \,/\, \alpha\,[CO_2] \quad \text{— (A.72)}$$

$$K_{2Y} = \gamma\,[H^+]\,[CO_3^=] \,/\, [HCO_3^-] \quad \text{— (A.73)}$$

$$H'(CO_2) = [CO_2] \,/\, p(CO_2) \quad \text{— (A.74)}$$

Derivation of expressions for calculating $p(CO_2)$ and $p(H_2S)$

Define

$$A = m\,x(H_2S) - H'(H_2S)\,p(H_2S)$$

$$B = m\,x(CO_2) - H'(CO_2)\,p(CO_2)$$

and

$$z = [RR'NCOO^-]$$

Neglecting $[H^+]$, $[OH^-]$, $[CO_3^=]$ and $[S^=]$ in the conservation equations, and using the above notation,

$$[HS^-] = m\,x(H_2S) - [H_2S] = m\,x(H_2S) - H'(H_2S)\,p(H_2S) = A$$

$$[HCO_3^-] = m\,x(CO_2) - [CO_2] - [RR'NCOO^-] = m\,x(CO_2) - H'(CO_2)\,p(CO_2) - z = B - z$$

$$[RR'NH_2^+] = [HCO_3^-] + [RR'NCOO^-] + [HS^-] = B - z + z + A = A + B$$

$[RR'NH] = m - [RR'NH_2^+] - [RR'NCOO^-] = m - z - A - B$

Multiply Equations (A.5), (A.7), (A.9) and divide by Equation (A.6). On rearrangement, we get

$$p(H_2S) = (K_w / K_iK_{1C}H'(H_2S))\,(\gamma^2 / a\alpha)\,A(A + B) / (m - z - A - B) \quad \text{— (A.75)}$$

Rearranging Equation (A.10),

$$p(CO_2) = (\gamma^2 / a^2\alpha^2K_M)\,z\,(A + B) / (m - z - A - B)^2 \quad \text{— (A.76)}$$

Multiply Equations (A.5), (A.11), (A.13) and divide by Equations (A.6), (A.10) to get

$$K_iK_{1Y}H'(CO_2) / K_wK_M = (B - z)(m - z - A - B) / az \quad \text{— (A.77)}$$

After some manipulations,

$$A = m - z - B - (K_iK_{1Y}H'(CO_2) / K_wK_M)\,z / a(B - z)$$

When $[CO_2] \ll [HCO_3^-] + [RR'NCOO^-]$ and $[H_2S] \ll [HS^-]$,

$$A = m\,x(H_2S)$$

$$B = m\,x(CO_2)$$

$$z = B - [HCO_3^-] = m\,x(CO_2) - [HCO_3^-]$$

Substitute in Equations (A.14) and (A.15) to obtain

$$p(H_2S) = (K_w / K_iK_{1C}H'(H_2S))\,(\gamma^2 / a\alpha) \times mx(H_2S)(x(H_2S) + x(CO_2)) / (1 - x(H_2S) - 2x(CO_2) + [HCO_3^-] / m) \quad \text{— (A.78)}$$

and

$$p(CO_2) = (\gamma^2 / K_Ma^2\alpha^2) \times (x(H_2S) + x(CO_2))(x(CO_2) - [HCO_3^-] / m) / (1 - x(CO_2) - 2x(H_2S) + [HCO_3^-] / m)^2 \quad \text{— (A.79)}$$

Substitution in Equation (A.16) gives

$$mx(H_2S) = m - (mx(CO_2) - [HCO_3^-]) - mx(CO_2) - (K_1 / a)(mx(CO_2) - [HCO_3^-]) / [HCO_3^-]$$

where

$$K_1 = K_iK_{1Y}H'(CO_2) / K_wK_M$$

Multiply the equation by $[HCO_3^-] / m^2$ and rearrange.

$$([HCO_3^-] / m)^2 + ([HCO_3^-] / m)(1 - x(H_2S) - 2x(CO_2) + K_1 / am) - K_1x(CO_2) / am = 0$$

$$\therefore [HCO_3^-] / m = - 0.5(1 - x(H_2S) - 2x(CO_2) + K_1 / am) \pm ([0.5(1 - x(H_2S) - 2x(CO_2) + K_1 / am)]^2 + K_1x(CO_2) / am)^2$$

To determine the sign of the discriminant, consider the case where $x(CO_2) = 0$, $x(H_2S) = 0$ and hence $[HCO_3^-] = 0$. Negative sign of the discriminant leads to an absurd result, viz. $1 + K_1 / am = 0$. As K_1 / am is positive,

$$[HCO_3^-] / m = ([0.5(1 - x(H_2S) - 2x(CO_2) + K_1 / am)]^2 + K_1x(CO_2) / am)^{0.5} - 0.5(1 - x(H_2S) - 2x(CO_2) + K_1 / am) \quad \text{— (A.80)}$$

When $[HCO_3^-] \ll [RR'NCOO^-]$, Equations (A.17) and (A.18) reduce to

$$p(H_2S) = (K_w / K_iK_{1C}H'(H_2S))\,(\gamma^2 / a\alpha)\,mx(H_2S)(x(H_2S) + x(CO_2)) / (1 - x(H_2S) - 2x(CO_2)) \quad \text{— (A.81)}$$

$$p(CO_2) = (\gamma^2 / K_Ma^2\alpha^2) \times x(CO_2)(x(H_2S) + x(CO_2)) / (1 - x(H_2S) - 2x(CO_2))^2 \quad \text{— (A.82)}$$

When $x(CO_2) = 0$, $z = 0$, $B = 0$ and Equation (A.14) becomes

$$p(H_2S) = (K_w / K_iK_{1C}H'(H_2S))\,(\gamma^2 / a\alpha)\,A^2 / (m - A)$$

Define $K'' = (K_w / K_iK_{1C})\,(\gamma^2 / a\alpha)$

$\therefore p(H_2S) = (K'' / H'(H_2S))A^2 / (m - A)$

Substitute $A = mx(H_2S) - H'(H_2S)p(H_2S)$, expand and rearrange to get

$w^2 + w(1 - x(H_2S) + 2K''x(H_2S)) = K''(1 - K'')x^2(H_2S)$

where $w = (1 - K'')p(H_2S)H'(H_2S) / m$. The solution to this equation is

$w + 0.5(1 - x(H_2S) + 2K''x(H_2S)) = \pm ([0.5(1 - x(H_2S))]^2 + K''x(H_2S))^{0.5}$

The sign of the discriminant has to be positive. (Consider the case $x(H_2S) = 0$, $p(H_2S) = 0$.)

$\therefore w = ([0.5(1 - x(H_2S))]^2 + K''x(H_2S))^{0.5} - 0.5(1 - x(H_2S) + 2K''x(H_2S))$ — (A.83)

and $p(H_2S) = wm / H'(H_2S)(1 - K'')$.

The corresponding result for the case $x(H_2S) = 0$ can be derived as follows:

Define $K_1 = (K_1K_{1Y}H'(CO_2) / K_w) \cdot (a\alpha^2 / \gamma^2)$

and $K_2 = (K_MK_w / K_1K_{1Y}H'(CO_2)) \cdot a$

$\therefore K_1K_2 = K_Ma^2\alpha^2 / \gamma^2$

In this notation, Equations (A.15) and (A.16) become

$p(CO_2) = (1 / K_1K_2) \cdot zB / (m - z - B)^2$

$0 = m - z - B - z / [K_2(B - z)]$

To eliminate z from these equations, expand to get

$z^2 - z(m + (1 / K_2)) + B(m - B) = 0$

$\therefore z = 0.5(m + (1 / K_2)) \pm ([0.5(m + (1 / K_2))]^2 - B(m - B))^{0.5}$

When $m = 0$, $z = 0$ and $B = 0$ (i.e. no CO_2 present),

$0 = (1 / 2K_2) \pm ([1 / 2K_2]^2)^{0.5}$

As $K_2 > 0$, the sign of the discriminant must be negative.

$\therefore z = m/2 + 1/2K_2 - ([B - m/2 - 1/2K_2]^2 + B/K_2)^{0.5}$

Now $p(CO_2) = (1 / K_1K_2) \cdot zB / (m - z - B)^2$

and $m - z - B = z / K_2(B - z)$.

$\therefore p(CO_2) = (B / K_1) \cdot (z - B) / (z - m + B)$

Substituting the expression for z,

$p(CO_2) = (B / K_1)) \cdot (Q + 0.5m - B) / (Q - 0.5m + B)$ — (A.84)

where $Q = (1 / 2K_2) - ([B - 0.5m - 0.5 / K_2]^2 + B / K_2)^{0.5}$

But $B = mx(CO_2) - H'(CO_2)p(CO_2)$. These two equations can be solved for B and $p(CO_2)$.

Determination of K_{1Y}

When $x(H_2S) = 0$, $x(CO_2) = 0.5$, Equations (A.18) and (A.19) become

$p(CO_2) = 0.5\gamma^2 / (K_Ma^2\alpha^2) (0.5 - [HCO_3^-] / m) / ([HCO_3^-] / m)^2$

$[HCO_3^-] / m = ([K_I / 2am)]^2 + K_I / 2am)^{0.5} - K_I / 2am$ where $K_I = K_1K_{1Y}H'(CO_2) / K_wK_M$

Substituting this expression in the equation for $p(CO_2)$,

$p(CO_2) = 0.5K_wm\gamma^2 / K_1K_{1Y} H'(CO_2)a\alpha^2$

$\therefore K_{1Y} = 0.5m\gamma^2K_w / p(CO_2)a\alpha^2K_1H'(CO_2)$ — (A.85)

Tertiary amines do not form carbamates. An equation similar to Equation (A.24) can be obtained for moderate loadings by neglecting $[H^+]$, $[OH^-]$, $[CO_2]$ and $[CO_3^=]$ in the balance equations.

$[HCO_3^-] = mx(CO_2) - [CO_2] = B$

$[RR'NH_2^+] = [HCO_3^-] = B$

$[RR'NH] = m - [RR'NH_2^+] = m - B$

Multiplying Equations (A.5), (A.11), (A.13) and dividing by Equation (A.6),

$$K_iK_{1Y}H'(CO_2) \;/\; K_w = (\gamma^2/a\alpha^2)\cdot B^2/[(m - B)p(CO_2)]$$

As $[CO_2] \ll [HCO_3^-]$, $B = [HCO_3^-] \cong mx(CO_2)$.

$$\therefore K_{1Y} = mx^2(CO_2)\gamma^2K_w \;/\; p(CO_2)(1 - x(CO_2))a\alpha^2K_iH'(CO_2) \qquad \text{— (A.86)}$$

Determination of K_M for primary and secondary amines

For moderate loadings, Equations (A.18) and (A.19) hold with $x(H_2S)$ set equal to zero. These can be solved for K_M by trial and error. (Assume K_M. Calculate K_I, $[HCO_3^-]/m$, $p(CO_2)$ and check against the experimental $p(CO_2)$. Repeat till the predicted and the experimental $p(CO_2)$ are same.)

Determination of K_{1C}

Consider the system H_2S / amine / water. For moderate loading, Equation (A.17), with $x(CO_2) = 0$, gives

$$p(H_2S) = (K_w/K_iK_{1C}H'(H_2S))\cdot(\gamma^2/a\alpha)\cdot mx^2(H_2S) \;/\; (1 - x(H_2S))$$

$$\therefore K_{1C} = (K_w/p(H_2S)K_iH'(H_2S))\cdot(\gamma^2/a\alpha)\cdot mx^2(H_2S) \;/\; (1 - x(H_2S))$$

APPENDIX B

Brown's Method

In this Appendix, Brown's method of solving a system of nonlinear equations is described. The method has been discussed in detail by Brown (1969), Brown and Dennis (1971) and Brown (1973). Brown's method is based on a partial pivoting technique similar to Gaussian elimination.

Consider the following system of algebraic equations:

$$f_1(\mathbf{x}) = f_1(x_1, x_2, \ldots, x_N) = 0$$
$$f_2(\mathbf{x}) = f_2(x_1, x_2, \ldots, x_N) = 0$$
$$\ldots$$
$$f_N(\mathbf{x}) = f_N(x_1, x_2, \ldots, x_N) = 0$$

or, in vector form, $\mathbf{f}(\mathbf{x}) = \mathbf{0}$.

In Newton's method, the functions are expanded simultaneously about a point $\mathbf{x}^n$ assumed to be close to the solution $\mathbf{x}^*$.

$$\mathbf{f}(\mathbf{x}) = \mathbf{f}(\mathbf{x}^n) + \mathbf{J}(\mathbf{x}^n)\cdot(\mathbf{x} - \mathbf{x}^n) + \text{Higher order terms}$$

$\mathbf{J}$ is the Jacobian matrix defined by $J_{ij} = \partial f_i/\partial x_j$. When $\mathbf{x}$ is close enough to $\mathbf{x}^n$, the higher order terms are negligible. If it is assumed that $\mathbf{x}$ is a close approximation to $\mathbf{x}^*$, so that $\mathbf{f}(\mathbf{x}) \cong \mathbf{0}$,

$$\mathbf{0} = \mathbf{f}(\mathbf{x}^n) + \mathbf{J}(\mathbf{x}^n)\cdot(\mathbf{x} - \mathbf{x}^n)$$

Solving for $\mathbf{x}$,

$$\mathbf{x}^{n+1} = \mathbf{x} = \mathbf{x}^n - \mathbf{J}^{-1}(\mathbf{x}^n)\cdot\mathbf{f}(\mathbf{x}^n)$$

Thus starting with a guess $\mathbf{x}^0$, one can solve iteratively for $n = 0, 1, 2, \ldots$. When the partial derivatives $\partial f_i/\partial x_j$ are estimated by the first difference approximation, the method is called the discrete Newton's method. In this method,

$$\partial f_i/\partial x_j \cong [f_i(\mathbf{x}^n + h^n\mathbf{e}_j) - f_i(\mathbf{x}^n)]/h^n$$

where $\mathbf{e}_j$ is the j-th unit vector and h^n is chosen so that $h^n \ll \| \mathbf{f}(\mathbf{x}^n) \|$.

Brown's method handles the functions one at a time and uses the information obtained from working with f_1 while working with f_2, etc.. This successive substitution nature of Brown's method is similar to Gaussian elimination for linear systems. Numerical stability of this method is improved by partial pivoting as described below.

Brown's method requires fewer function evaluations, $(N^2+3N)/2$, as compared to Newton's method which requires (N^2+N) evaluations in each step. The method is at least second order convergent. This means that the number of significant digits approximately doubles in each iteration. The method consists of the following steps:

Step 1. Expand the first function f_1 in a Taylor series expansion around $\mathbf{x}^n$. Ignoring the higher order terms,

$$f_1(\mathbf{x}) = f_1(\mathbf{x}^n) + \Sigma\, f_{1,x(j),h}(\mathbf{x}^n)\cdot(x_j - x_j^n)$$

where

$$f_{1,x(j),h}(\mathbf{x}^n) = [f_1(\mathbf{x}^n + h\,\mathbf{e}_j) - f_1(\mathbf{x}^n)] \,/\, h$$

Define

$$f_1^n = f_1(\mathbf{x}^n)$$

and

$$f_{1\,x(j),h}^n = f_{1,x(j),h}(\mathbf{x}^n)$$

If $\mathbf{x}$ is close enough to $\mathbf{x}^*$, $f_1(\mathbf{x}) \cong 0$. Thus we can solve for that variable, say x_N, whose corresponding derivative $f_{1\,x(N),h}^n$ is the largest in absolute value.

$$x_N = x_N^n - (f_1^n / f_{1\,x(N),h}^n) - \Sigma\,(f_{1\,x(j),h}^n / f_{1\,x(N),h}^n)\cdot(x_j - x_j^n)$$

The constants $(f_1^n / f_{1\,x(N),h}^n)$ and $(f_{1\,x(j),h}^n / f_{1\,x(N),h}^n)$ are stored for future use. Here x_N is a linear function of the N-1 variables $x_1, x_2, \ldots, x_{N-1}$. Rename the left hand side as $L_N(x_1, x_2, \ldots, x_{N-1})$

$$\therefore\ x_N = L_N(x_1, x_2, \ldots, x_{N-1}).$$

Also define $L_N^n = L_N(x_1^n, x_2^n, \ldots, x_{N-1}^n)$.

Step 2. Define a function g_2 of the N-1 variables $x_1, x_2, \ldots, x_{N-1}$ as follows.

$$g_2(x_1, \ldots, x_{N-1}) = f_2(x_1, \ldots, x_{N-1}, L_N(x_1, \ldots, x_{N-1}))$$

and

$$g_2^n = f_2(x_1^n, \ldots, x_{N-1}^n, L_N^n)$$

Now expand g_2 in a Taylor series and solve for that variable, say x_{N-1}, whose corresponding derivative $g_{2\,x(N-1),h}$ is the largest in magnitude.

$$x_{N-1} = x_{N-1}^n - (g_2^n / g_{2\,x(N-1),h}^n) - \Sigma\,(g_{2\,x(j),h}^n / g_{2\,x(N-1),h}^n)\cdot(x_j - x_j^n)$$

Define the right hand side as $L_{N-1}(x_1, \ldots, x_{N-2})$.

Step 3. Define

$$g_3(x_1, \ldots, x_{N-2}) \equiv f_3(x_1, \ldots, x_{N-2}, L_{N-1}, L_N)$$

where $L_{N-1} \equiv L_{N-1}(x_1, x_2, \ldots, x_{N-2})$

and $L_N \equiv L_N(x_1, x_2, \ldots, x_{N-2}, L_{N-1})$.

The process in Steps 1 and 2 is repeated and the variable, say x_{N-2}, whose corresponding derivative $g_{3\,x(N-2),h}$ is largest in magnitude is written as

$$L_{N-2}(x_1, x_2, \ldots, x_{N-3}).$$

In this way, each step adds one linear equation to the linear system. During (k+1)-st step, it is necessary to evaluate g_{k+1} ($\equiv f_{k+1}$) for various arguments. These arguments are obtained by back-substitution in the system $L_N, L_{N-1}, \ldots, L_{N-k}$ which has built up.

Step N. Here we have $g_N \equiv f_N(x_1, L_2, \ldots, L_N)$

which is a function of the single variable x_1. Expand g_N, linearize, and solve for x_1.

$$x_1 = x_1^n - g_N^n \,/\, g_{N\,x(1),h}^n$$

The point x_1 obtained from this expression is used as the next approximation x_1^{n+1} to the first component x_1^*. The complete L_j system is back-solved to get improved approximation to $x_2^*, \ldots, x_N^*$.

Here

$$x_j^{n+1} = L_j(x_1^{n+1}, \ldots, x_{j-1}^{n+1})$$

The details on convergence theorems, choice of h etc may be found in the references cited above.

APPENDIX C

Computer program

The computer program described in Chapter IV is available upon request from the Department of Chemical Engineering, The University of Alberta, Edmonton, Alberta, Canada. A flow chart of this program is presented on the next page.

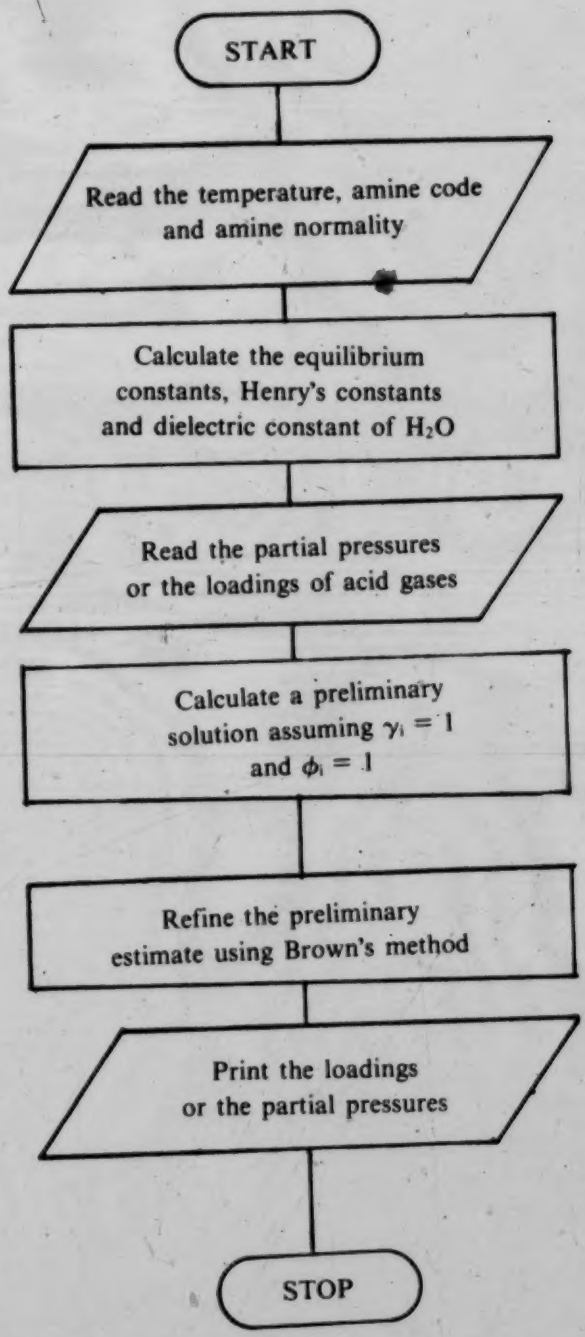
START
Read the temperature, amine code and amine normality
Calculate the equilibrium constants, Henry's constants and dielectric constant of H_2O
Read the partial pressures or the loadings of acid gases
Calculate a preliminary solution assuming $\gamma_i = 1$ and $\phi_i = 1$
Refine the preliminary estimate using Brown's method
Print the loadings or the partial pressures
STOP

Figure 28. Flow chart for the computer program